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Synthesis and Characterization of ZIF-8 and ZIF-8/polymer composites

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Abstract

In this project we carried out a systematic study into the synthesis of ZIF-8 using different experimental conditions to find the most suitable ZIF-8 particle morphologies. We then investigated the preparation of aligned porous ZIF-8-polymer composites via the freeze drying method. For the purposes of our project, we decided that particles between 100nm and 2um would be a suitable size for the preparation of polymer composite materials. And smaller would lead to the particles not being visible in the polymer framework and any larger they would be difficult to disperse homogenously throughout the framework. We used several different methods from literature, finally focusing on a method that was used by Cravillon which used an auxiliary ligand to modulate their reaction. The two auxiliary ligands were sodium formate and 1-methyl imidazole.

We used water as the solvent to prepare these size-controllable ZIF-8 particles. This was carried out in a much lower volume of solvent than the corresponding methanol reactions. We carried out a systematic study into a wide range of conditions wrt 2-MeIM and 1-MeIM concentration as well as temperature- using room temperature, heating the reaction and solvothermal conditions. Three ZIF-8 conditions were identified as being promising for taking forward and these were all in water 1:20:20 Zn:2-MeIM:1-MeIM RT ~350nm, 1:10:2 80C ~400nm and 1:3:1 80C ~2.5um. The 1:3:1 had a very low conc of 2-MeIM and formed interesting nano-aggregate particles.

We then investigated the preparation of aligned porous ZIF-8-polymer composites via the freeze drying method. These three particles were used to prepare aligned porous ZIF-8@PSS composite materials with three different ratio's of ZIF:PSS 1:1, 1:3, and 3:1. These were directionally frozen in liquid nitrogen slowly ~1mm/10 seconds and then placed in a freeze drier to sublime the solvent and leave the porous structure intact. These structures were all successful and we characterised the two most successful, 1:2:20 and 1:10:2 for the BET surface area, pore size and volume and BJH average pore size. For 1:20:20 RT 3:1 ZIF-8:PSS we found a BET surface area of 440m squred per gram. This reduced as the ratio of zif:pss decreased as expected. The 1:10:2 case had a larger surface area of 521 m squared per gram. These two composite structures were aligned porous frameworks with high surface areas and tunable particle sizes. The next steps would be to test them for the applications.

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MOF	Metal Organic Framework
PCP	Porous Coordination Polymer
SBU	Secondary Building Unit
PSM	Post-Synthetic-Modification
ZIF	Zeolitic Imidazolate Framework
Im	Imidazolate
SOD	Sodalite
2-MeIM	2-Methyl imidazole
DEF	N,N-diethylformamide
NMP	1-methyl-2-pyrrolidone
DMF	Dimethylformamide
MTBS	Methyltributylammoniumsulfate
INA	Isonicotinic Acid
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
BET	Brunauer-Emmett-Teller
TGA	Thermogravimetric Analysis
1-MeIM	1-Methylimidazole
PVP	Polyvinylpyrrolidone
PAM	Polyacrylamide
PSS	Polystyrene sulphonate
RT	Room Temperature

Chapter 1- Introduction to porous materials, MOFs, ZIFs and synthetic methods

1.1 Porous Materials

Research into the area of porous materials has been of great interest for a long time due to their potential applications in drug delivery, separation of gases, storage of guest molecules and catalysis.[1] Highly ordered, crystalline materials containing pores are perfect for use in these applications. There are three types of porous materials and they are defined by the sizes of their pores. These are microporous, mesoporous and macroporous materials. The size of the pores affects the material's properties and therefore their suitability for use in different applications. This makes it very important that the class of material is defined, as can be seen in *Figure 1*.

***Figure 1**- Size scale of porous materials*

Metal Organic Frameworks (MOFs), zeolites and Zeolitic Imidazolate Frameworks (ZIFs) are just some examples of 3-Dimensional porous materials which have received a lot of attention due to their high surface areas, large pore volumes and relative stability.

Microporous materials are a very important class of crystalline compound that contain interconnected cages and cavities or channels with pores of ~2.5-20 Å which is comparable to molecular dimensions. The distribution of pore sizes in this class of materials tends to be relatively small. The arrangement of the channels and cavities defines whether the pore system in the material is 1-dimensional, 2-dimensional or 3-dimensional.[2] These materials have properties including large internal surface areas and pore volumes giving values typically of more than $300 m^2 g^{-1}$ and $0.1 cm^3 g^{-1}$ respectively.[2] The large internal surface areas make these highly reactive materials when there are functional groups on the surface which is useful for applications such as catalysis and also separation. The very uniform nature of the micropores mean these materials are able to separate molecules based on their size and shape, or shape selectivity, and gives them the name 'molecular sieves'. This shape selectivity can be used in

many applications including forms of chromatography and in ‘shape-selective’ catalysis. In these applications the microporous material controls either which reactant molecules can enter the pores or which products can leave. It can also control the geometry of the transition state of the molecule, restricting the types of reaction that can take place.

Zeolites are microporous crystalline aluminosilicates with well-defined structures which have been used as catalysts in the petrochemical industry for decades. They are the catalyst in the cracking process of petrochemicals, water purification and also for the separation of gases.[3] They occur naturally as minerals and can also be made synthetically. Zeolites were first synthesised in 1862 by Deville via a hydrothermal synthesis and the single crystal structures of zeolite minerals were first reported by Taylor and Pauling in 1930.[4-7] They are made up of three-dimensional, interconnecting frameworks of AlO_4 and SiO_4 connected through bridging oxygens and there are over 150 different types of framework. The framework structure contains channels, pores and cavities that can store guest molecules. Their pore sizes can range from 3Å to an upper limit of 10Å. Reactions can take place inside the cavities, making them attractive for applications such as catalysis and gas separation. The microporous nature of zeolites is what makes them suitable for these applications as they selectively adsorb or exclude certain molecules depending on their size or shape, which is needed for molecular sieving and also for shape-selective catalysis.

A drawback of using zeolites is that they have very rigid structures and there is a limit to the variety of structure and functionality that is available.

1.2 MOFs

Metal organic Frameworks (MOFs), sometimes known as porous coordination polymers (PCP's), are highly ordered crystalline materials which are prepared by the self-assembly of metal ions with organic linkers (***Figure 2***). These linkers are organic structures and include tri-carboxylic acids, pyridyl groups and imidazoles.

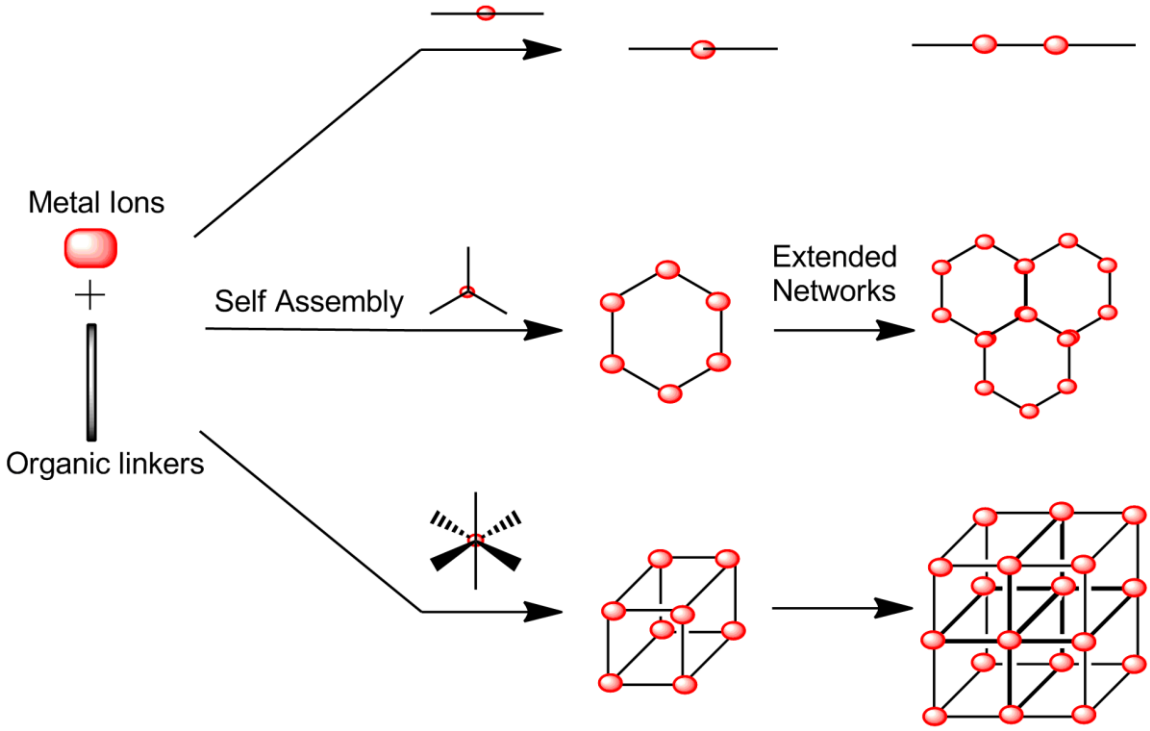


Figure 2- Metal organic framework synthesis of 1D, 2D and 3D networks, from metal ions and organic linkers.

MOFs have many attractive properties such as diverse topology, very low density, high porosity, tuneable pore size of molecular dimensions and high surface areas.[8] They are also easily functionalized through altering the metal, organic linker or secondary building unit (SBU). The introduction of organic components into the framework of these microporous materials also endows the materials with increased hydrophobicity. These properties make them of high interest for numerous applications including the normal uses of porous materials in catalysis and gas storage and separation which are becoming increasingly important due to

environmental concerns, and which are based on pore size and shape, and also biomedical applications and use in sensors.[8-11] The choice of metal ion or organic ligand is very important as this can affect the framework topology, the pore size and shape of the particles and therefore the overall chemical functionality of the structure.[12] The ability to rationally design MOF structures at the molecular level is a very interesting property and the added functionality can be built into the structure or can be added post-synthetically by post-synthetic modification (PSM) reactions and can give the MOFs additional properties for specific applications, for example, magnetism, luminescence and chirality.[2, 12-16] The simplest way of adding functionality is to use a functional component, either the metal or the organic linker. This can be used to incorporate a certain amount of active centres into a usually inactive framework, to give a material properties needed for catalysis and separation.[2] A net charge can also be incorporated into the framework by choice of metal ions used. This is seen in aluminosilicate zeolite materials and it gives the materials Brönsted acidity properties. Changing the length of the organic linker has been shown to increase pore size which is favourable for applications such as gas storage as it increases the adsorption capacity and desorption rates.[17]

MOFs are favoured over zeolites for many applications because of their inherent flexibility which is caused by the inorganic-organic hybrid nature of their frameworks. This endows them with very unique adsorption and desorption characteristics and much larger pore volumes than seen for solely inorganic frameworks.[2] They are much more easily functionalized than zeolites or cross-linked polymers.[18] They are also relatively easy to prepare, the most common methods being solvothermal or hydrothermal methods in various solvents including water, and they are also mostly air stable and insoluble in normal organic solvents as well as being relatively resistant to high temperatures due to the strong nature of the metal-organic bonds.[19]

MOFs became of interest around 1990, when Hoskins and Robson published their paper foreseeing the formation of a wide range of stable, microporous, crystalline solids which would have catalytic, ion-exchange and gas sorption properties and the possibility of post-synthetic modification by the addition of functional groups. [20, 21] The term MOF however was first introduced by Yaghi et al in 1995 when he used hydrothermal synthesis to produce a copper MOF with a layered structure.[14, 19] Some of the most studied MOFs are MOF-5, which is a Zn MOF, and HKUST-1 which is a Cu MOF, and these are shown in ***Figure 3*** along with some other much investigated MOFs.[22-24]

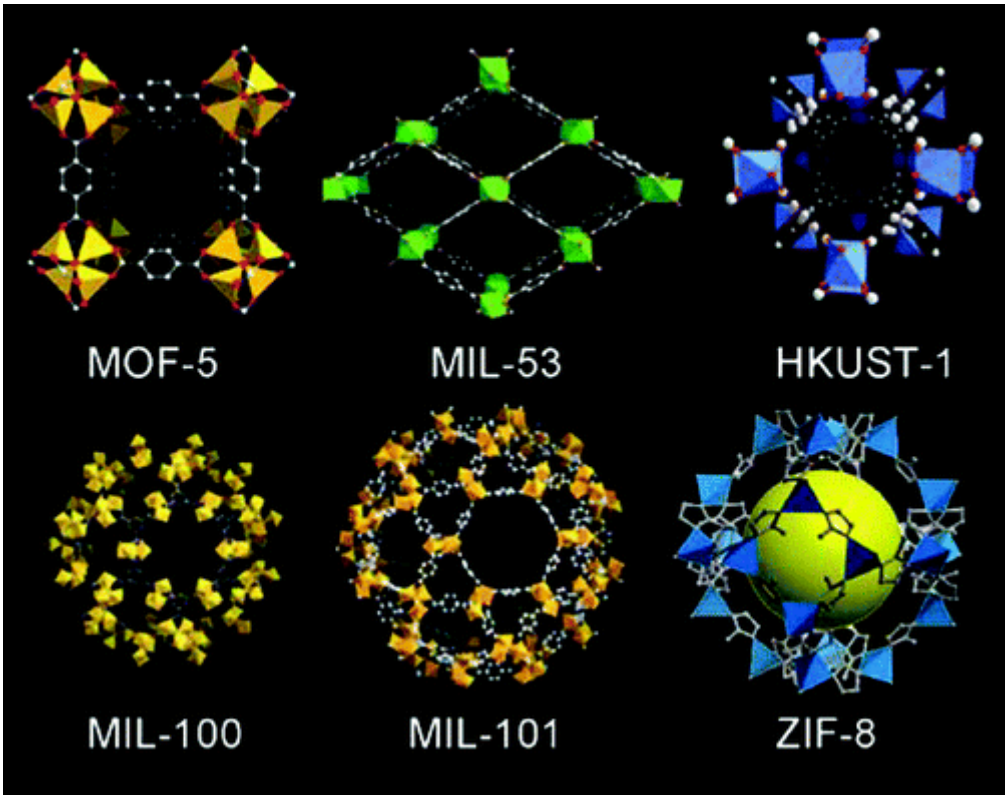


Figure 3- *Structures of some well-studied MOFs showing the pore sizes.*[24]

The crystalline nature of MOFs allows them to be studied by X-ray diffraction, a method which allows the structure of the framework to be fully understood with the position of each individual atom in space defined. This knowledge of the structure of MOFs allows for more precise control over modification of size, shape and morphologies.

Although MOFs and zeolites seem to look very promising for many applications there is the problem of the fact that they are mostly not stable in polar solvents or strong acids/bases and they are usually microporous which limits gas delivery rates and adsorption capacity and desorption rates. MOFs also have limited thermal stability as it is dependent on their relatively weak metal-ligand bonds compared to their inorganic counterparts.[2]

To combat these problems there is a desire to incorporate micropores as well as mesopores and macropores into a framework structure. There are many shapes and sizes accessible to MOFs achieved by the alteration of the metal ion, the organic linker, solvent used, concentration of reactants, temperature and any other variables.

1.3 ZIFs

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOF which have attracted attention as they combine the highly desirable properties of both zeolites and MOFs such as microporosity, crystallinity and high surface area and also high chemical and thermal stability.[9, 25, 26] They will be the main focus of our study.

Many different ZIFs have been reported, usually having a metal ion, zinc or cobalt, coordinated through nitrogen to imidazolate linkers to form a neutral framework with tuneable nanopores. The pores are formed by the presence of ZnN_4 or CoN_4 tetrahedral clusters. Their pores and channels allow access of guest molecules for applications such as gas storage and catalysis and they can differentiate between molecules at a molecular level, for use in separation of gases.

The reason for their name is due to the structure of their framework being very similar to that of zeolites, with the tetrahedral silicon or aluminium with bridging oxygen are replaced by Zn or Si bridged by Im. The bond angles in both cases are 145°, shown in ***Figure 4***.[25]

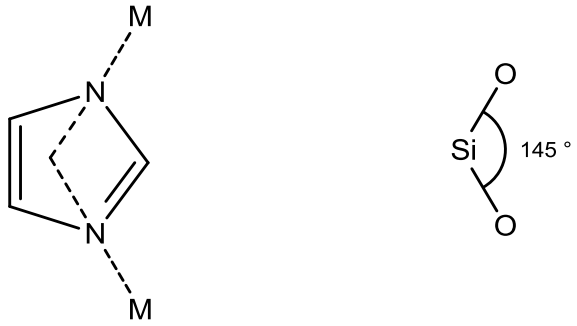


Figure 4*- The bridging angle in both ZIFs and zeolites is 145°*

The imidazolate linker can vary and some examples are shown in ***Figure 5***. The additional functional groups can give the ZIFs added functionality for specific applications.

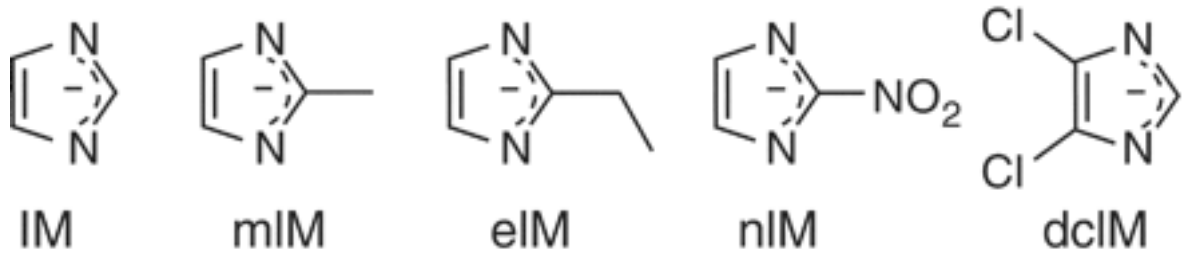


Figure 5- *Some imidazole linkers used in ZIF synthesis. IM= imidazolate, m-IM= 2-methyl imidazolate, eIM= ethyl imidazolate, n-IM=nitro imidazolate, dcIM= dichloro imidazolate.*[9]

ZIFs are much more flexible than zeolites due to the inorganic-organic structure and the functionalized imidazolate linkers. This makes their structures and pore sizes much more easy to control and so allows more accessible tuning of the ZIF properties.

One of the most studied ZIFs is ZIF-8 which is made up of Zn tetrahedral clusters and 2-Methyl imidazolate linkers and prepared using zinc hexanitrate and 2-methyl imidazole. It has the sodalite (SOD) type of zeolite structure and forms a truncated octahedron shown in ***Figure 6***. These join together to make an extended 3D framework as seen in ***Figure 7***.[25] ZIF-8 was first reported by Yaghi et al using solvothermal synthesis in 2006.[25] ZIFs have remarkable chemical stability in refluxing organic solvents, water and aqueous alkaline solution which is unlike any other MOF previously investigated.

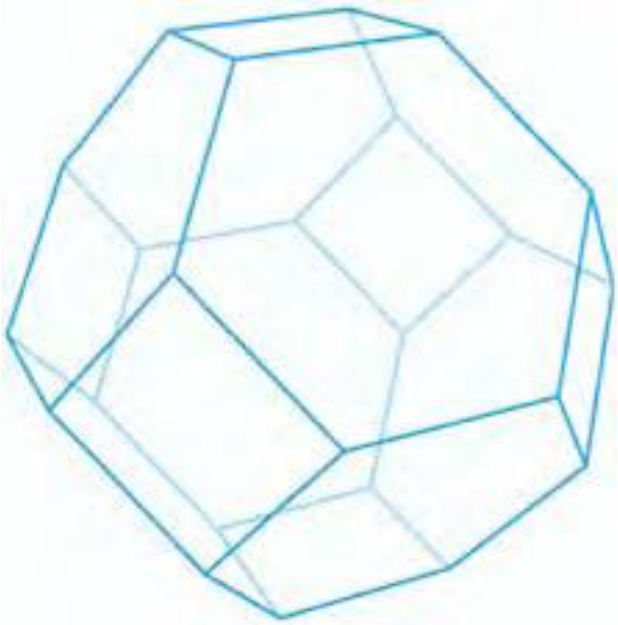


Figure 6*-Sodalite unit cell forming a truncated octahedron.*[27]

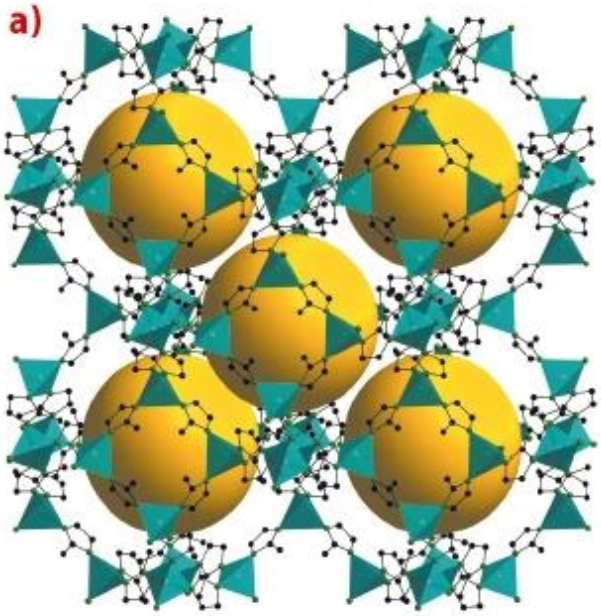


Figure 7*- Structure of ZIF-8, yellow spheres indicate the pore volume.*[25]

ZIF-8 has pores of diameter 11.6 Å and pore openings of 3.4 Å due to the methyl side chains on the imidazolate linkers. This gives them pore sizes approximately double that of zeolites, as the imidazolate linker is longer than that of the bridging oxygens in zeolites, but apertures that are comparable to the smallest of molecular sieves.[25]

ZIFs have very large surface areas, and in Yaghi's original experiment he found ZIF-8 to have a Brunauer-Emmett-Teller (BET) surface area of 1630 m^2/g which is much higher than any value found for zeolites.

ZIF-8 is insoluble and stable in methanol and water even when placed under reflux, resisting hydrolysis, which is not found for other zinc MOFs. This remarkable stability has been suggested to be for two reasons the first being that the bond between the imidazolate N and the M(II) ion is comparable in strength to that of covalent solids, and the second is that the hydrophobic pore of ZIFs repels water molecules hence eliminating the chance of attack of water on the MIm_4 (M=Zn/Co) tetrahedral units.[25] This hydrophobic character that endows the ZIF-8 with such exceptional stability is very beneficial in terms of applications, with the ZIF-8 being able to withstand harsh chemical and thermal environments. As well as all these other attractive properties they have been found to have good adsorption affinities with hydrogen and methane.[28-30] This gives them the ability to separate H_2 and methane from other larger molecules.

The properties of ZIFs, such as high thermal and chemical stability, make them favourable over other MOFs and zeolites although there are advantages and disadvantages to all these materials for applications industrially.[31]

1.4 Synthetic procedures

In the synthesis of MOFs and ZIFs the main goal is to find the ideal conditions so as to form the inorganic building blocks without degrading the more chemically and thermally sensitive organic linker component and also to allow nucleation and crystallization to produce the correct phase of the framework structure.[8] The fact that all these requirements must be met satisfactorily means that exploratory methods of synthesis are still being employed for many MOFs and this has led to the use of high throughput methods, often used in the pharmaceutical industry, to be adopted.[16, 32-34] This allows the synthesis to be optimized as well as a high density of information to be obtained in a relatively short period of time. But high throughput methods don't give any more information into the process of crystallization, for which characterization techniques must be used.[8]

Research into MOF formation and crystallization must be carried out to increase understanding of the process of MOF formation so that optimised procedures can be developed. Through much investigation into MOF synthesis it has been found that different synthesis methods, starting from the same mixture of reagents, can give different MOFs, different morphologies, particle shapes and particle sizes, and also distribution of particles.[8, 32, 34] Changing variables such as the concentration of reactants, order of addition, solvent concentration, pH, whether the reaction mixture is agitated during the reaction, the addition of any auxiliary ligands and reaction time, to name just a few, can have a remarkably large effect on the structure and morphology of the particles formed.[2, 34, 35] For example, the reaction temperature can affect the structure of the MOF particles, with increased reaction temperature often leading to more dense structures.[8, 36] These differences in the MOFs then affect the properties of the particles and hence their use in certain applications. For example, small particles are needed for the formation of membranes and sonochemical or microwave-assisted methods are often utilized, but also the formation of thin-films uses a substrate onto which MOFs are deposited or grown in a tightly packed layer.[8] Different morphologies and structure types are needed for applications in specific areas, as well as crystal size and shape, for example to make thin films, spheres, nanoparticles, membranes, monolayers and microfibers, and all of these need different synthetic methods to be employed.[8] As well as this, work has been done on changing the pore size of the MOFs from microporous to larger pores and mesopores.[8, 37-41] This changes the ability of the MOF to uptake or release molecules and also affects the host-guest interactions within the framework structure.

1.4.1 Traditional methods

The interdisciplinary approach to research into MOFs has led to a diverse range of synthetic procedures based on both coordination chemistry and crystal engineering and also procedures used by zeolite chemists. Coordination chemistry tends to use quite mild conditions as weak interactions are usually expected. Whereas zeolite chemists use harsh conditions with high temperatures and pressures in their methods. This means that there is a great variation in the conditions employed to make MOFs, with large differences in reaction temperatures and reaction vessels used and many strategies being adopted by different research groups.[8] There are many approaches to MOF synthesis stemming from these two areas of chemistry, with electrochemical and mechanochemical syntheses and also in situ linker synthesis being introduced by coordination chemists, while solvothermal and microwave-assisted syntheses and the use of structure directing agents as components of the framework have been brought to the table by zeolite chemists.[3, 8, 18] The review by Stock et al[8] (2011) gives an account of the different synthesis methods that have been applied in the last 20 years. These include methods such as room temperature synthesis, conventional electric heating, microwave heating, electrochemistry, mechanochemistry and ultrasonic methods. The method chosen is related to the desired morphology of the MOF products, with certain strategies being chosen to control shape and size of the MOF or to give certain structures such as thin films or membranes.

1.4.1.1 Solvothermal

A wide range of experimental conditions are used to synthesize MOFs and other porous materials. Solvothermal reactions have been widely used in the synthesis of porous materials as well as for other materials such as magnetic and electronic compounds and also catalysts. MOFs have traditionally been made by solvothermal methods which utilizes conventional electric heating.[2, 8, 32]

The definition given by Rabenau[42] in his review on hydrothermal synthesis states that solvothermal reactions are reactions taking place in closed vessels under autogenous pressure above the boiling point of the solvent.[8, 42] Solvothermal synthesis is a method used often to grow single crystals, and it uses an autoclave which is a thick walled steel vessel (***Figure 8***). The autoclave is placed under high temperatures and pressures typically of 80-250°C and 3-90MPa respectively.[2] Many different solvents have been used in this type of synthesis including methanol, water and DMF.[19] The reactions can range from several hours to ~30days.

These methods can often be very time consuming and complicated in nature for example, Yaghi et al[19] produced a copper MOF though hydrothermal synthesis which consisted of heating the reaction vessel to 140°C at a rate of 5 degrees/minute and holding it there for 24 hours. They then cooled it at 0.1 degree/minute to 90°C and held it there for 12 hours. And they then finally cooled it down to room temperature at 0.1degree/minute which would take a further 90 minutes. This produced an air-stable compound that was insoluble in water and other common organic solvents. Their study found that hydrothermal synthesis was a successful route to producing crystalline, zeolite-like materials.[19]

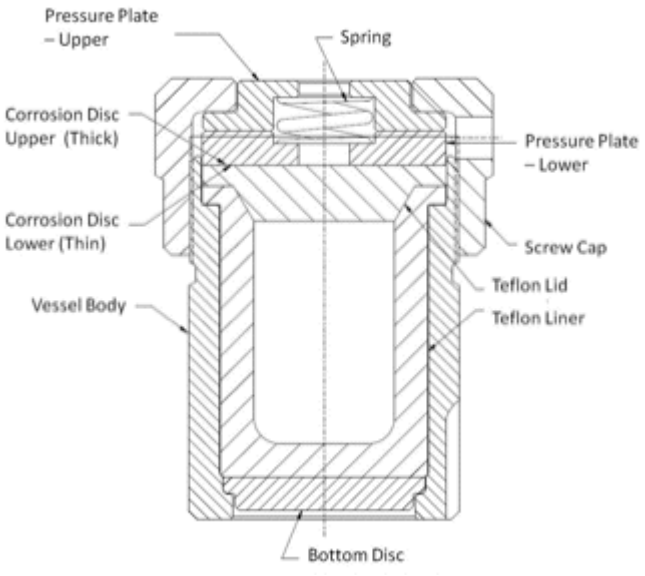


***Figure 8**-Autoclave for solvothermal synthesis*[8]

Studies have been carried out into the effect of changing parameters such as pH, temperature, concentration and reaction time, and how these effect the morphology of the particles produced.[36] High throughput methods have been used to allow for large amounts of results to be obtained with only a small volume of reactants being consumed and a smaller time scale as it uses a parallel reactor which can run many reactions simultaneously.[9] These studies have discovered some trends in the way morphology changes with certain parameters, for example, Forster et al investigated the way a cobalt MOF changed with temperature and they found that the structures become more dense as the temperature increases.[36]

Generally, ZIF-8 has been synthesised via hydrothermal or solvothermal methods by the reaction of zinc nitrate with 2-Methylimidazole (2-MeIM) in solvents like DMF, methanol or water.[25, 31] Typically the hydrated metal salt is used, for example $Zn(NO_3)_2.6H_2O$, with an imidazolate linker and in the past an amide solvent was usually used e.g. N,N-diethylformamide (DEF). A study by Park et al[25] investigated the hydrothermal synthesis of twelve ZIF species and in their method they heated the solutions of zinc nitrate and imidazolate in amide solvent to temperatures around 150°C and ZIF particles precipitated after 48-96 hours. These particles were easily isolated and characterized. The ZIF-8 produced was thermally and chemically stable in boiling benzene, methanol and water for 7 days.[25] It was also stable in 8M sodium hydroxide at 100°C for up to 24 hours. This is therefore shown to be a remarkably resilient framework, with great promise for many applications as it can withstand harsh conditions and hydrolysis under very strong reaction conditions.

High throughput syntheses have also been used in the solvothermal synthesis of ZIFs, seen in the study by Banerjee et al[9], and has been found to yield pure phase tetrahedral ZIF structures. They undertook a synthesis of 25 ZIF structures and the reactions were scalable to multigram amounts without changing the reaction conditions, and the thermal and chemical stability of the ZIFs was very good.

1.4.1.2 Nonsolvothermal or room temperature syntheses

These are reactions taking place at or below the boiling point of the solvent and at ambient pressure. This is a much simpler approach to MOF synthesis and can be split into reactions at room temperature or at elevated temperatures. This allows for the procedures to be cheaper and simpler and more energy efficient, with high temperatures and pressures being avoided. Some very well-known MOFs have been obtained at room temperature, surprisingly just by mixing the starting materials, which is also called direct precipitation and takes place in a very short space of time.[8, 36] Some examples of these are MOF-5, HKUST-1 and ZIF-8.[23, 43, 44] Increased reaction temperatures change the framework structures and usually result in more dense structures.[36] This increase in temperature is sometimes necessary to allow efficient reaction rates and rates of crystallization.

Although ZIF-8 is usually synthesised by solvothermal methods it has also been found that ZIF-8 can be prepared at room temperature in many solvents including both methanol and water if an excess of 2-MeIM, relative to the Zn reagent, is used.[43] This can be done simply by

mixing the starting materials, without even stirring the solution. This has been found for some of the well-known MOFs including HKUST-1 and ZIF-8.[26, 43, 44] The reactions also tend to be a lot shorter with some methods, using aqueous solvents, taking only minutes compared to hours/days for methods using non-aqueous or solvothermal methods.[26]

Room temperature synthesis of ZIF-8 was investigated by Cravillon et al[43] and they made monodisperse, pure phase ZIF-8 without the need for any stabilizing ligands or the use of any activation methods e.g. conventional heating, microwave or ultrasound irradiation. They used methanol as the solvent and an excess of 2-MeIM with a ratio of Zn:2MeIM:MeOH of 1:8:700. The ZIF-8 produced was on the nanoscale and stable up to ~200°C, therefore less thermally stable than microscale ZIF-8 which is stable up to about 400°C.[43]

The ability to produce pure-phase nanoscale ZIF-8 in a quick, cheap and simple method with a narrow polydispersity is much more favourable over other more costly and time consuming procedures that involve high pressures and therefore could be more dangerous. These ZIF-8 can be produced cheaply as precursors for structures such as membranes and ZIF films.[43]

1.4.2 Alternative synthesis routes

There is often a form of energy inputted into a reaction to make it take place, usually via heating in solvothermal or non-solvothermal synthesis. MOF synthesis is generally carried out in a solvent, e.g. Methanol, at temperatures between 25°C and 250°C, but the energy needed for the reaction to take place can come from other sources and therefore other methods of synthesis can be used.[45] Some examples of these alternate methods are Microwave-assisted synthesis, mechanochemical synthesis, sonochemical which uses ultrasound radiation, or Microfluidic synthesis. In each case the conditions, such as pressure, reaction time etc., are different and therefore the morphology of the particles produced will be different. This means that a certain synthetic route can be chosen to target a particular MOF framework morphology in order to get a MOF which exhibits certain properties suitable for a particular application.[8] For example, when MOFs are needed for biomedical applications, e.g. imaging, drug storage and drug delivery, they need to be nano-size and nontoxic and have high loading capacities, so must have large pore volumes.[46] This requires the use of microwave-assisted or ultrasound radiation methods to be used.

For MOFs to be made commercially available, synthetic routes have to be established that are fast, easy, cheap and can produce large amounts of MOF. So, different methods must be investigated to determine the most suitable routes for large-scale production.

1.4.2.1 Microwave assisted synthesis

Microwave irradiation has been used in synthetic chemistry for a long time but mostly in organic chemistry.[47] This method has only recently been used in the synthesis of porous materials and MOFs. The basis of this method is the interaction of the electromagnetic waves with mobile electric charges in the reaction mixture. In solution these mobile electric charges come from polar solvent molecules or ions which try to align themselves to the electromagnetic field, and when an appropriate frequency is applied this causes collisions between the molecules and an increase in kinetic energy (KE) in the system. The increase in KE causes a temperature increase that is dispersed as the molecules collide and that is homogenous throughout the system.[48] In a solid the mobile charges come from electrons or ions in the solid and when the microwave radiation is applied an electric current is formed which causes heating due to resistance of the solid.[8]

This is a very effective method of heating throughout a system; however care must be taken when choosing the solvents as the microwave radiation interacts directly with the molecules in the system. This also means the amount of microwave radiation applied to the system must be controlled and this is the most important parameter in microwave-assisted synthesis.[8, 48]This method has the advantage of short reaction times, fast kinetics of nucleation and crystal growth and high-yields of products that are attractive for their proposed applications and can be readily isolated. There are also little or no secondary products so the particles produced are very pure without much purification needed to make them suitable for use. However there are concerns over the safety of this method and also the reproducibility of the particles formed as the morphology and phase purity of the particles can vary dramatically if the reaction conditions are not controlled strictly enough. This in turn affects the properties of the particles and their viability for use in applications.[38, 47, 48]

Many MOFs, some known and some never produced previously, have been prepared by microwave-assisted synthesis including MOF-5 and IRMO- 2 and -3.[8]

High-throughput methods have also been used in microwave synthesis of MOFs to reduce reaction time and amount of reagents used. They also, like solvothermal synthesis, tend to run at temperatures over 100°C.

Choi et al[49] investigated the common MOF, MOF-5, in microwave-assisted synthesis for the use in CO_2 capture and storage. They used this technique to improve the large scale production of the MOF, as it allows direct heating of the molecules, uniformly throughout the system causing rapid and even heating. When the desired products are microporous materials such as MOFs, this allows for homogeneous nucleation and a significant decrease in the length of time taken for crystallization when compared to conventional electric heating techniques, as used in normal solvothermal synthesis. Their method took only 30 minutes to produce high quality MOF-5 crystals compared to 24 hours when using traditional heating methods. They also used 1-methyl-2-pyrrolidone (NMP) as their solvent as it is much cheaper than traditionally used DEF, which again is due to their desire to make a large scale route to MOF production.[49] The size of the crystals produced were about 20-25μm which is about 20 times smaller than those prepared by conventional heating, but this is a common size difference when comparing microwave-assisted methods to conventional heating methods.[49, 50] Their product also had a slightly lower surface area than the MOF-5 produced by conventional heating methods due to the slight oxidation of the NMP used, which then makes it harder to remove from the pores of the framework. This also resulted in a slight brownish colour of the microwave-assisted product. They carried out a systematic study comparing the MOF-5 crystal formation at different microwave heating timescales, temperatures, ratios of Metal:Ligand and solvent concentrations, in order to optimize the procedure. They found that prolonged reaction time led to deterioration of the product with surface defects forming. In most cases the reduction of reaction time, as a result of changing reaction conditions, led to a reduction in crystal quality.

Bux et al[28] used a microwave-assisted solvothermal method to synthesise ZIF-8. They managed to reduce the reaction time to 4 hours with the use of microwave-assisted heating and the ZIF-8 they prepared was in the form of a membrane for gas separation and it was selective for hydrogen over other gases (***Figure 9***).

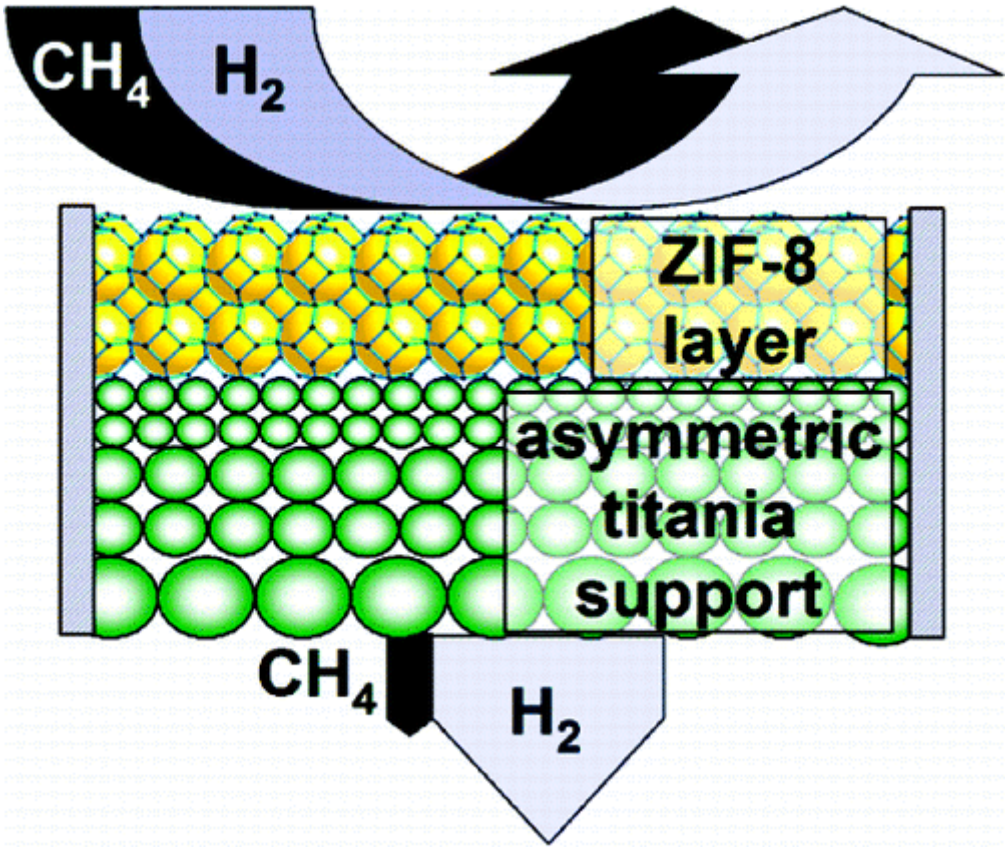


***Figure 9**-ZIF-8 membrane on a ceramic support shows selectivity for hydrogen over other gases.*[28]

Their membrane was however still relatively thick and further optimization would be needed to improve the hydrogen permeation of the membrane. They also used a different solvent to traditional syntheses, exchanging dimethylformamide (DMF) or aqueous methanol for pure methanol. This is because the polar methanol can be removed much more readily from the ZIF-8 pore system than DMF, as it interacts weakly with the framework.[28]

So, the use of microwave heating in order to reduce reaction time does seem to have its advantages, especially for large scale production of MOFs, however, the loss of crystal quality makes this method less attractive for certain applications.

1.4.2.2 Electrochemical Synthesis

Electrochemical synthesis has been adopted by some researchers for the preparation of MOFs as a method of excluding anions, for example nitrate or chloride, from the reaction mixture with the aim to improve the reactions for large-scale production in industry.

Electrochemical synthesis uses the metal ions and adds them to a solution containing the organic linker and a conducting salt. This process allows the production of MOFs to be carried out in a continuous process and it also has the ability to give a higher yield of MOF product than normal batch synthesis which is used in traditional solvothermal methods.

Both copper and zinc based MOFs have been prepared via this method in studies done by researchers at BASF. These include HKUST-1 and ZIF-8 with surface areas of ZIF-8 giving values of 1746m^2g^{-1}. Other work has been done on HKUST-1 by Schlesinger et al[51] comparing 6 different methods of MOF synthesis including solvothermal, microwave-assisted, electrochemical, ultrasonic and mechanochemical. In their procedure they include an additive to increase the conductivity for electrolysis e.g. methyltributylammoniumsulfate (MTBS) or Et_3N. These however tend to become incorporated into the framework structure and block the pores even when very effective activation procedures are used to clear the pores. The electrochemical route, in their paper, when compared to the other methods seems to be the least effective route to HKUST-1 preparation, with low yields, low surface areas and poor crystallinity. They found that the most successful route in their study was via microwave-assisted synthesis which had the shortest reaction time and produced pure HKUST-1 in reasonable yield high BET surface area of 1499 m^2g^{-1}.[51]

Electrochemical synthesis, although having attractive advantages such as continuous processing and therefore high yields, seems to give an inferior product and therefore other methods are favoured.

1.4.2.3 Mechanochemical synthesis

Mechanochemical force, or grinding, can be used to start chemical reactions by mechanical breakage of chemical bonds which is then followed by some kind of chemical change. It has been used in MOF synthesis since 2006 by Pichon et al in their solvent free approach to MOF synthesis.[52] Their method consisted simply of grinding the metal salt and the ligand together for ten minutes without any heating and resulted in the formation of the MOF [$Cu(INA)_2$] (INA

= Isonicotinic acid). Previous to their work, mechanochemical methods had only been used to produce non-porous coordination polymers; however they report the preparation of a crystalline, 3-dimensional microporous framework in quantitative yield. The by-products of water and acetic acid can be removed simply by heating the resulting mixture. X-Ray powder diffraction was used to characterize the compound and showed a highly crystalline framework with no remaining starting material.[52]

This solvent-free approach is very attractive for a number of reasons. One of the biggest reasons is the environmental advantage of the method with the opportunity for green large-scale production with the use of large quantities of unpleasant solvents being avoided. This also makes it a safer route compared to the traditional solvothermal route which uses organic solvents and high temperatures. As well as this there is the benefit of the absence of any solvent molecules in the framework or pores of the MOF structures. The reaction times are also usually very short, around 10-60 minutes, which is dramatically shorter than the solvothermal synthesis procedures. And although Pichon et al[52] used the metal salt and formed the acetic acid by-product, this can be avoided by the use of the metal oxide which generates water only, making it an even more efficient process.[8]

Liquid-assisted grinding (LAG) is the addition of minute amounts of solvent and has been shown to increase reaction rate.[53] The liquid can also behave as a structure-directing agent. This method has been used by Beldon et al[54] in the synthesis of ZIF-8. They used zinc oxide rather than the metal salt usually used. They demonstrated the time-dependent ZIF transformation through the variation of reaction time and they produced both porous and non-porous materials. Previous work on the mechanochemical preparation of ZIF-8 had found that only nonporous $Zn(2\text{-MeIM})_2$ was formed upon grinding and only when a large excess of 2-MeIM was used. Their work confirmed this and therefore they adopted the LAG methodology. They also managed to prepare ZIF-8 in the absence of liquid when using an ammonium salt additive.

1.4.2.4 Sonochemical synthesis

The application of high-energy ultrasound to a reaction mixture is the basis of sonochemical synthesis. The high-energy ultrasound is an oscillating sound pressure wave with a frequency between 20 kHz and ~10 MHz, so is not within the limit of human hearing, which is less than 20 kHz.[8] Ultrasound is used in many different areas, for example it can be used to measure

distances, or for ultrasound imaging in medicine. But it is also used to accelerate chemical processes. This is not due to direct interactions between the ultrasound and the molecules, as the wavelength is larger than the molecular dimensions. It is in fact due to the interaction of the ultrasound with the solvent liquid forming cyclic areas of low and high pressure. This results in the build-up of ultrasonic energy in bubbles which form, grow and collapse in a process called cavitation. Cavitation is associated with a fast release of energy with incredibly fast heating and cooling rates with very high temperatures and pressures in isolated areas.[8] There are many factors that can be varied which will affect this process, including which frequency of ultrasound is used and the intensity of this, which solvent is used as these will have different viscosities and chemical reactivities, the temperature chosen and the atmosphere in which the reaction is carried out. [55]

This area has not yet been greatly explored in MOF synthesis but there has been some research done. These research groups have focused on trying to find energy efficient and fast methods of MOF synthesis that are also environmentally friendly and involve no conventional electric heating. This is to make the reaction routes more favoured for large scale and industrial production, to reduce costs and to make the processes more efficient.[8] For many applications of MOFs, nanoscale crystals are required, and it is generally known that the particles produced via sonochemical methods are nanosize.

These reactions haven't been well reported as the reaction setup is not always included and also the statement that they are carried out at room temperature is not strictly true as the equipment always heats up after being on for some time. The fact that the setup is not recorded is important as the intensity of the ultrasound being applied to the system will strongly depend on the equipment used. Also the reactions can't be directly compared unless they are carried out using the same equipment. As well as this, some papers published have only characterized their "MOF" particles using one characterization technique, when there should be several techniques applied to get an accurate picture of the resulting particles.

The paper by Schlesinger et al[51] found that, although when using the ethanol/water mixture as solvent the ZIF-8 particles had a higher BET surface area, all the particles produced had poor crystallinity and a reduced yield.

As there are currently many limitations to this technique there must be further work carried out to ensure the reaction parameters can be more effectively controlled before it is used in systematic studies of MOFs.[55]

There are other types of synthetic procedure that have been tried in the synthesis of MOFs, for example microfluidic synthesis, however these are the main routes that have been studied.[33]

1.5 Characterization techniques

There are many characterization techniques used in the area of porous materials to determine the different aspects of their properties and structures. Complementary characterization techniques must be used to get a detailed picture of the MOFs as small changes in synthetic routes can lead to large changes in the MOFs morphologies and properties.[8, 56]

The most important of these techniques is powder X-Ray Diffraction (XRD) which is an analytical technique used to reveal information about the crystal structure of the materials investigated at an atomic and molecular level. XRD is carried out by concentrating an X-Ray beam on a crystalline material and observing the scattering intensity as a function of incident and scattered angle. This then allows the crystallographer to produce a 3-dimensional image of the material being imaged. The initial measurement of the scattered X-Ray and intensities gives an X-Ray diffraction pattern which can be compared to a known database of crystalline compounds and the compound can then be identified, as long as it's been synthesised previously and fully characterized.[57] For example, ZIF-8 has a recognisable XRD pattern, so when synthesising ZIF-8 using a new method in a new study, the XRD pattern of the product can be compared to that of the known ZIF-8 XRD pattern, and the preparation of ZIF-8 can be confirmed. This can be seen in ***Figure 10***, where an experimental XRD pattern is being compared to a simulated pattern from the known pattern of ZIF-8.

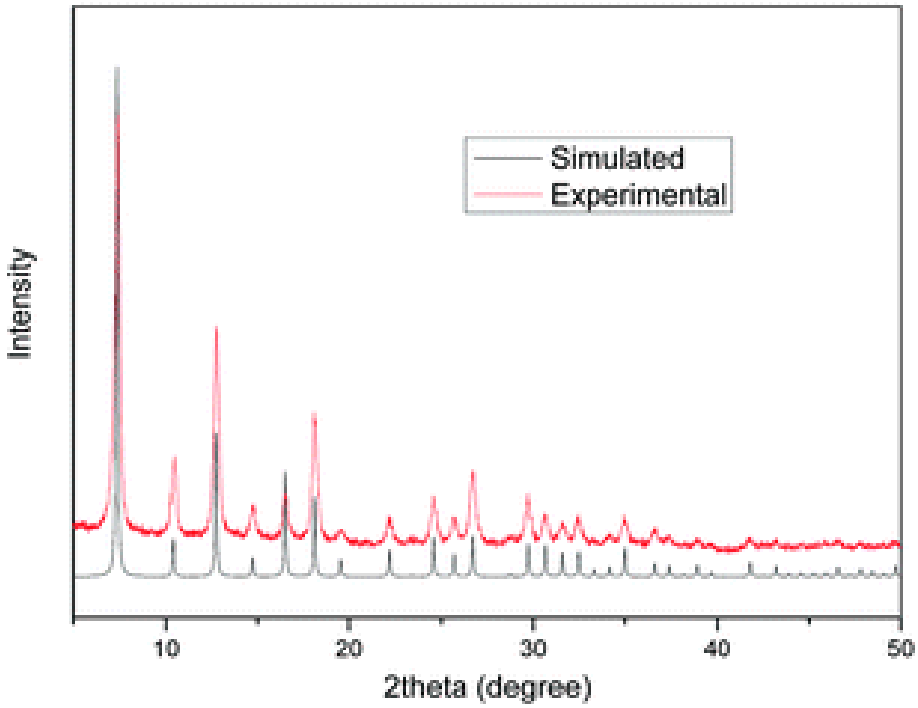


***Figure 10**- Comparison of experimental result to simulated pattern from known ZIF-8 pattern.*

Another important technique is electron microscopy. This uses an electron microscope which directs a beam of electrons at a material and produces an image in of this object that has been magnified many times. Electron microscopes can resolve an image much more effectively than a standard light microscope and is therefore used for small materials such as nano- or micro-scale and for porous materials where the pores are of interest to be imaged. When characterizing porous materials and MOFs in particular, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) are both adopted. SEM imaging is generally slightly poorer at resolving images than TEM however it can give an image of a bulk sample and also gives a very good representation of the 3-dimensional shape of the material. TEM tends to need very thin samples of only about 100 nm to be effective, which is difficult to do with delicate or brittle samples. Samples also need to be coated with a heavy metal atom, usually gold, for imaging to be successful. SEM is an effective way of getting a picture of the shape and size of the particles produced and is very useful in MOF synthesis.

The surface area and pore volume are also very important parameters to characterize in a porous material as the size and volume of the pores can greatly affect the materials properties and processability for applications. This is generally done by measuring the Brunauer-Emmett-Teller (BET) surface area of the material.[58] BET measurements use an adsorption isotherm which is based on physisorption and the ability of a gas to become weakly attached to the outside surface of a material when they come into contact. Physisorption is a reversible process and therefore a gas can adsorb and desorb easily to the surface of the material. The amount of gas that is adsorbed at a series of different pressures, at constant temperature, is measured to give the adsorption isotherm. The temperature is generally held constant using liquid nitrogen so the temperature is ~77K. The amount of gas adsorbed is plotted against the relative pressures and this gives the graph called the adsorption isotherm. The shape of the curve on the graph gives insight into the type of pores the material has. These shapes can be seen in ***Figure 11***, where some common isotherms are shown.

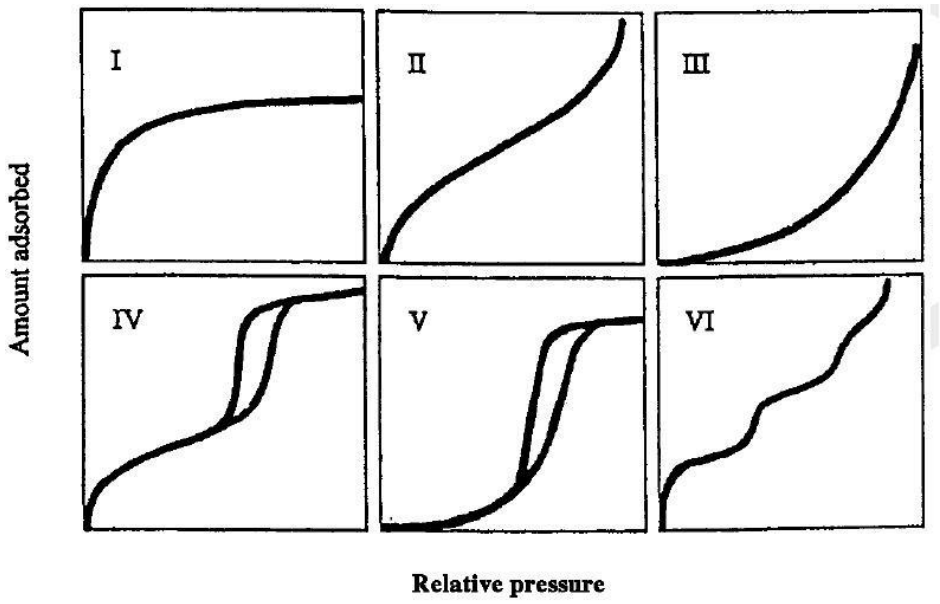


Figure 11*- Adsorption isotherms for BET surface area measurements.*

For porous materials I, IV and V are typically found and for MOFs with micropores Type I is the shape of the isotherm in most cases.

Most commonly the gas used for surface area determination is nitrogen however sometimes other gases are used, e.g. Argon or Carbon Dioxide.

The method used by Brunauer, Emmett and Teller uses the BET equation:

$$\frac{\mathbf{1}}{\boldsymbol{W}\left(\left(\frac{\boldsymbol{P_0}}{\boldsymbol{P}}\right)-\mathbf{1}\right)}=\frac{\mathbf{1}}{\boldsymbol{W_m C}}+\frac{\boldsymbol{C}-\mathbf{1}}{\boldsymbol{W_m C}}\left(\frac{\boldsymbol{P}}{\boldsymbol{P_0}}\right)$$

Where W= weight of gas adsorbed

P/P_0= relative pressure

W_m= weight of adsorbate as monolayer

C= BET constant and is:

$$\boldsymbol{C}=\boldsymbol{exp}\left(\frac{\boldsymbol{E_1}-\boldsymbol{E_L}}{\boldsymbol{RT}}\right)$$

Where E_1= heat of adsorption for 1st layer

E_L= heat of adsorption for second and higher layers (heat of liquefaction)

R= gas constant (8.314 $JK^{-1}mol^{-1}$)

T= temperature

For the plot on the graph $1/[W(P/P_0)-1]$ is plotted against P/P_0.This gives a slope and intercept of:

$$\boldsymbol{slope, s}=\frac{(\mathbf{C}-\mathbf{1})}{\boldsymbol{W_m C}}$$

$$\boldsymbol{intercept, i}=\frac{\mathbf{1}}{\boldsymbol{W_m C}}$$

And then: $$\boldsymbol{W_m}=\frac{\mathbf{1}}{\boldsymbol{s+i}}$$

Then total surface area is derived by the equation:

$$\boldsymbol{S_t}=\frac{\boldsymbol{W_m N A_{CS}}}{\boldsymbol{M}}$$

Where N= Avogadro's number ($6.023x10^{23}$)

M= Molecular weight of adsorbate

A_{CS}= Adsorbate cross sectional area (16.2 $Å^2$ for Nitrogen)

The specific surface area can finally be derived by total Surface area divided by weight of the sample.[58]

An important step before measurement of surface area is to degas the sample; this consists of creating a vacuum and heating the sample to relatively high temperatures in order to remove all gas from the pores before the adsorption isotherm is measured. The apparatus used to measure the BET surface area can also be used to determine the pore volume of the material which is another important piece of data needed to characterize the porous compounds if they are being investigated for their applications.

In this project XRD, BET surface area determination and SEM imaging will all be used together to characterize the materials synthesised.

1.6 Project Outline

In this project we carried out a systematic study into the synthesis of ZIF-8 using different experimental conditions to find the most attractive ZIF-8 particle morphologies for the preparation of polymer composite materials. By this we mean particles that are not too small, so they are easily visible in the polymer structures but also not too big as they would be less easily dispersed in the polymer solution. The particles which have very nicely defined shapes and low polydispersity are also more favoured. The different chemical conditions included changing concentrations of reactants and solvents, the addition of auxiliary ligands and variation of the concentration of this, temperature and reaction time. We then investigated the preparation of aligned porous ZIF-8-polymer composites via the novel freeze drying method.

Chapter 2- ZIF-8 synthesis in Methanol

2.1 Synthesis of ZIF-8

Synthesis of MOFs has generally been carried out using amide solvents such as diethyl formamide (DEF) and dimethylformamide (DMF) in solvothermal reactions. DMF in particular is an unpleasant solvent to use, with it being thought of as a possible carcinogen and also possibly having the ability to cause defects in foetus' or induce miscarriages in pregnant women.[59] They are also relatively costly and the synthetic procedures and reactions take quite long periods of time. There are also some workups of these reactions which use very nasty solvents for example, Park et al[25] used chloroform to separate the ZIF-8 particle they had formed in DMF from the waste material. Obviously this is not ideal, the use of a well-known extremely hazardous solvent, again with links to cancer, and reactions like these want to be avoided. To our knowledge, no ZIF-8 synthesis has been carried out in these solvents under non-solvothermal conditions. There have also been syntheses done in Methanol/amine solvent mixtures, but these tend to have long reaction times. For example, Huang et al[60] used a mixture of methanol and aqueous ammonia in their reaction procedure, and the synthesis took a month with the first particles taking several days to appear.[60]

The requirement in science and research in general, to reduce the cost of synthetic procedures and also the ever increasing importance of reactions being more environmentally friendly with regard to waste and energy used, has generated a need for new synthetic procedures to be developed. The use of methanol as a solvent rather than these amide solvents is an attractive prospect for reducing the cost and increasing the ease of these synthetic procedures. The use of methanol over DMF or methanol/solvent mixtures allows for the much more effective and efficient removal of the solvent molecules from the pores of the formed ZIF-8 particles. The much more easy removal of molecules from the pores allows for the porosity of the ZIF-8 particles to be greatly increased and this is an advantage for applications such as gas storage and separation. There are now several reported syntheses which use methanol as the solvent, in both solvothermal and non-solvothermal syntheses. The aim to further reduce cost and time scales means that room temperature syntheses are increasingly attractive for large-scale production of materials.

Venna et al[61] in their first study synthesised ZIF-8 in methanol following the solvothermal method but using pure methanol as the solvent. They stirred their mixture at room temperature

for 5 minutes before putting the solution into a Teflon lined autoclave and heating under autogenous pressure at 150°C for 5 hours. This method, although still using relatively high temperatures in the solvothermal route, is much less time intensive and has the added benefit of the cheaper solvent MeOH being used. Their XRD data showed the formation of pure-phase crystalline ZIF-8 with average crystal size of ~45 nm, calculated from the broadening of the XRD peaks. These particles were relatively monodisperse. The Type I isotherm indicated the microporous nature of their particles which had a BET surface area of 1072 m^2g^{-1}.

Cravillon et al[43] synthesised ZIF-8 in a room temperature synthesis using a ratio of 1:8:700 Zn:2-MeIM:MeOH. No stabilizing ligands were used or activation through e.g. conventional heating or microwave irradiation, and they produced ZIF-8 colloidal suspensions and powders. The excess of 2-MeIM was important, according to their findings, in order to get nanocrystals of ZIF-8. Comparison of their XRD data with known patterns of ZIF-8 showed that they had succeeded in producing pure-phase ZIF-8 with an average particle size of 46nm, estimated from the broadening of the peaks. Their ZIF-8 crystals had a narrow size distribution but their BET surface are of 962 m^2g^{-1} is lower than values found for microscale ZIF-8 particles in research by Yaghi in 2006.[25] Yaghi reported values of 1630 m^2g^{-1} for their ZIF-8 synthesised in a solvothermal reaction using DMF as solvent. This is attributed to the retention of some guest molecules in the pores of the ZIF-8 nanoparticles. However they have developed a cheap and quick synthesis route to make pure-phase ZIF-8 nanoparticles which have good thermal and chemical stability and a narrow particle size distribution.

Venna et al[62] in 2010 combined their previous method with the procedure described by Cravillon et al, and developed a room temperature ZIF-8 synthesis in pure methanol which used a ratio of 1:5 Zn:2-MeIM. They varied the timescale of their reactions, carrying out a study into the structural evolution of ZIF-8 particles. They left their longest reaction for 24 hours and the shortest was left for only 20 minutes.

Their analysis of the data collected indicated that the ZIF-8 was at over 90% crystallinity from 50 minutes onwards and stayed constant practically for the rest of the reaction time. Reaction times longer than 24hours did not affect the crystallinity therefore 24 hours were judged to be the point where ZIF-8 reaches maximum crystallinity. This study shows that short reaction times are possible for the synthesis of ZIF-8 pure-phase crystals when reactions are carried out in methanol at room temperature.

An interesting study was carried out by Cravillon et al[35], into the control of ZIF-8 crystal formation on the nano- and micro-scales. They produced nanocrystals with size range of 10-65nm and microcrystals with a size of ~1μm of prototypical ZIF-8 in a quick room temperature synthesis. The particle size was controlled by the use of auxiliary monodentate ligands in addition to an excess of the bridging bidentate 2-MeIM ligand. Several different monodentate ligands were investigated which had different functionalities and the effect they had on the ZIF-8 particle size was attributed to a combination of a modulation of the formation of the complex as well as of the deprotonation equilibria of the 2-MeIM during nucleation and growth of the ZIF-8 crystals. In-situ light scattering was adopted to monitor the way the auxiliary ligands affect the crystal growth process. The Ligands they investigated as modulating ligands were sodium formate, 1-methylimidazole and n-butylamine. They used a 1:4:X:1000 ratio of Zn:2-MeIM:auxiliary ligand:MeOH and were not stirred, were just left at room temperature for 24 hours. The value of X was varied to monitor the effect of the different concentrations of modulating ligand. Without any modulating ligand the pure-phase ZIF-8 produced had a particle size of~64 nm and a rhombic dodecahedral shape.

In the presence of sodium formate or 1-methylimidazole (1-MeIM) at X=4 the particles formed were found to be pure-phase ZIF-8 which still have the rhombic dodecahedral shape and have a remarkably small size distribution. They both seem to affect the ZIF-8 crystals in the same way although they are very different ligands in nature. The particles had very narrow size distribution and nice morphology. They both produce microparticles of 1-2μm in diameter.

When n-butylamine was used with X=4, particles of 18 nm in diameter were formed and they were almost spherical in shape. They then varied the ratios of the Zn:2-MeIM:n-butylamine:MeOH. Varying the molar ratios of these reagents resulted in changing of the ZIF-8 particle sizes.

They did not investigate the effect of changing the 1-MeIM or sodium formate concentration however, which would be interesting to explore further.

These are all very interesting new methods of ZIF-8 synthesis using cheap, fast and effective synthetic routes in methanol.

Our target was to make size-controlled ZIF-8 nanoparticles or microparticles in a systematic study in methanol under several different reaction conditions. These would be later employed to make ZIF-8/polymer composites. We aimed to find several ZIF-8 particles with different

particle sizes and morphologies within the size range we think is suitable. This is 100nm-2µm, as we think these particles are large enough to be visible in the polymer framework but not too large as to fall out of solution and therefore give an inhomogeneous dispersion. These particles were then carried forward into our further studies into composite materials. In previous studies on composite materials, the structure of the ZIF-8 particles has not been carefully considered and therefore the properties and function of the composites prepared wasn't being optimised for specific uses. In this study, the ability to precisely control the properties of the materials is very advantageous. The chemicals that will be used for this investigation are zinc nitrate hexahydrate, 2-methylimidazole, sodium formate and 1-methyl imidazole.

2.2 Results and Discussion

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) was simply mixed with 2-methyl imidazole (2-MeIM) in a 1:8 ratio and stirred for 16 hours at room temperature in methanol (1:8:430, Zn:2-MeIM:MeOH)). In this reaction the Zn^{2+} ion centres form a complex with the 2-MeIM linkers and form the well-known sodalite structure to give ZIF-8, as is shown in ***Figure 12.***

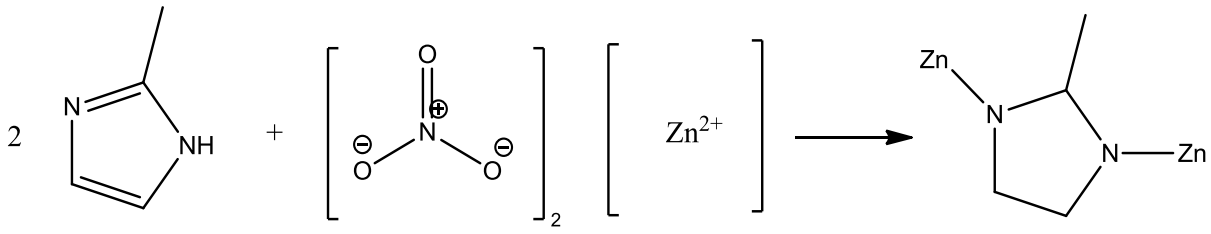


Figure 12*- A simple diagram to show complex formation between Zn ions and 2-MeIM linkers to give the sodalite ZIF-8 structure.*

ZIF-8 particles were formed in ~40% yield which was comparable to that seen previously, and the XRD pattern showed that pure-phase ZIF-8 had been successfully prepared. This can be seen in ***Figure 13***, with the inlay picture showing a typical ZIF-8 pattern. It can clearly be seen that the same peaks are present for our synthesised ZIF-8 and therefore the ZIF-8 framework has been synthesised.

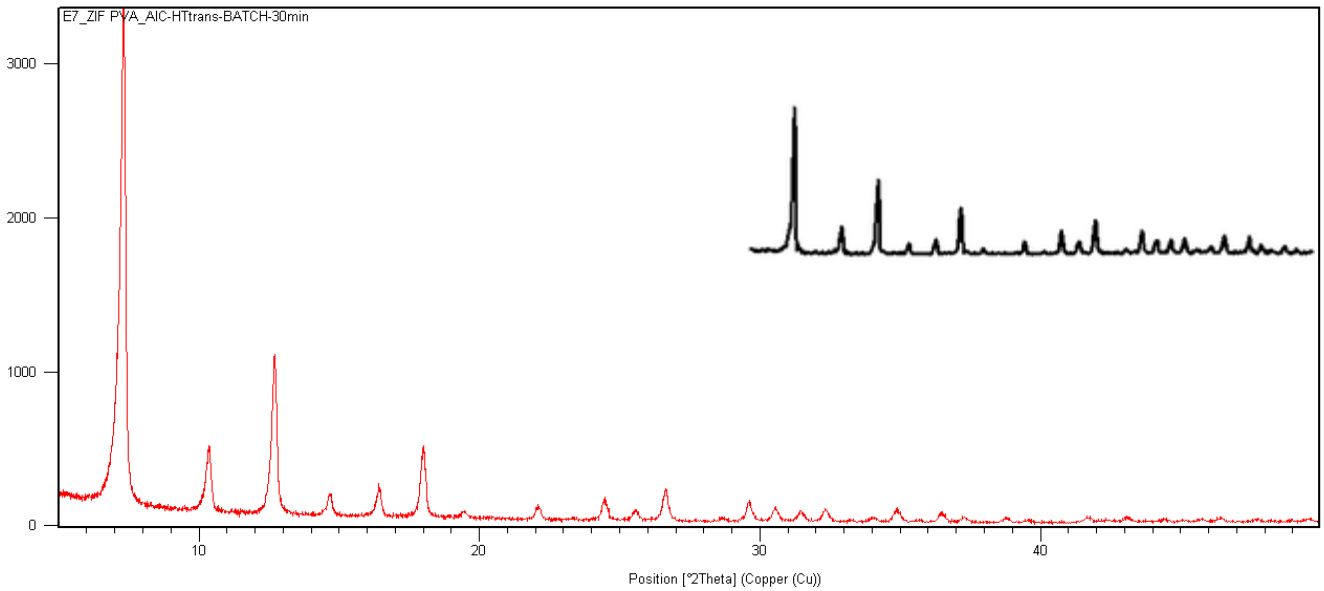


***Figure 13**- XRD pattern of ZIF-8 particles prepared using 1:8 ratio Zn:2-MeIM in MeOH.*

The particles formed were, however, much smaller than those previously reported, with average particle sizes 50 nm with some particles seeming to have aggregated (***Figure 14***).

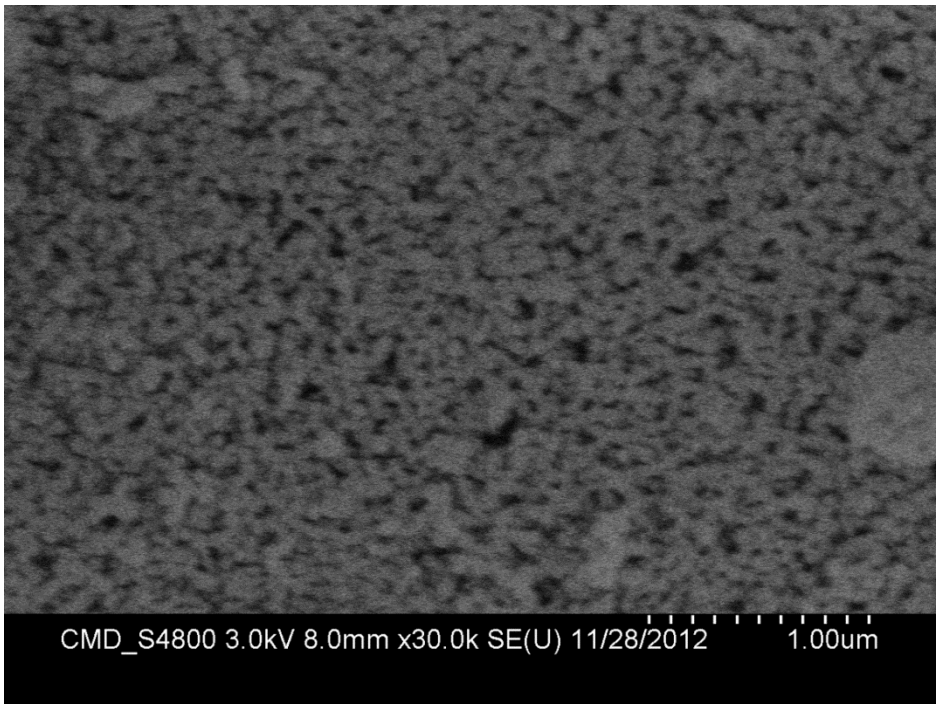


***Figure 14**-SEM image of particles prepared using the 1:8 ratio Zn:2-MeIM in MeOH. The particle sizes are ~50nm.*

These particles were not easy to get clear images of and therefore the actual morphologies of the particles cannot be identified. As the particles are very small, they would not be appropriate for use in composite preparation due to the difficulty to visualise them in the composite structures.

With this in mind, our research turned to finding a method of preparing ZIF-8 structures with controllable particle size so that the correct particles could be chosen for each application intended. The particle size range that was decided on was between 100 nm and 2 µm as this was an appropriate size for composite preparation.

Venna et al[62] reported the room temperature synthesis of ZIF-8 in MeOH using a 5:1 ratio Zn:2-MeIM and this resulted in the formation of pure-phase ZIF-8 with particle sizes of ~500 nm and with a relatively narrow size distribution. We decided to follow this procedure first and investigate if we could prepare larger ZIF-8 nanoparticles or size-controlled microparticles, which can then be easily observed by SEM imaging.

The reaction proceeded for 24 hours and produced ZIF-8 particles with a 38% yield, which is similar to that of the previous procedure, and with a particle size of ~100 nm. These particles were easier to see however they were not much bigger than those produced using the previous method, and therefore this procedure was not chosen as the standard for the investigation into size-controlled ZIF-8 particles.

Another paper which reports the preparation of larger ZIF-8 particles is written by Cravillon et al.[35] In their study they carried out a room temperature synthesis of ZIF-8 nano- and microcrystals by adopting a simple and straightforward method which uses an excess of the bidentate 2-MeIM as well as including a monodentate auxiliary ligand to control the crystal size. Their investigation involved varying the modulating ligand and also, in some cases the ratio of Zn:2-MeIM:modulating ligand:MeOH. They report that the size of the ZIF-8 particles in the absence of auxiliary ligand is ~65 nm and they have a rhombic dodecahedron morphology with narrow size distribution.

These particle sizes increased dramatically with the inclusion of sodium formate or 1-MeIM as auxiliary ligand to 1-2µm. They did not however carry out any study into the effect of varying the concentration of these two modulating ligands.

The procedure produced by Cravillon et al was used in this study. It adopts a 1:4:4:1000 ratio of Zn:2-MeIM:L:MeOH (L= Sodium formate or 1-MeIM). An unusual aspect of their

procedure is the fact that the reaction proceeds without stirring throughout the reaction, with stirring only occurring on the initial mixing of reagents. This was because, when they tried stirring, it resulted in a very wide range of particle sizes, which they attributed to secondary nucleation of the ZIF-8 particles. This lack of stirring means that the reaction method is even simpler, and more attractive if being scaled up for large-scale synthesis. A systematic study of the effect of the concentration of modulating ligand on the size of the ZIF- particles produced was carried out following this method by Cravillon et al. The different conditions that we used for this systematic study are summarised in ***Table 1***, along with some observations about the ZIF-8 particles prepared.

***Table 1**- ZIF-8 synthesis in MeOH + auxiliary ligands sodium formate and 1-MeIM*[35]

Sample	Conditions	Observations
ZIF-8 + Sodium formate	Following Cravillon et al method[35] Molar ratio Zn:2MeIM:Na:MeOH 1:4:4:1000 24hrs, room temp Stirred while mixing then turned off.	~1µm particle size, very monodisperse, nice particle morphology. XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 +1/2 Sodium formate	½ The amount in the paper and used in the reaction above	ZIF particles settled out of MeOH Quite polydisperse, sizes ranging from <500nm-1µm. XRD shows ZIF-8 pattern
ZIF-8 + 1/4 Sodium formate	1/4 The amount in the paper	ZIF particles settled out of MeOH Mostly cubes of about 300nm. Some big cubes- could we improve by doing 1/3? XRD shows ZIF-8 pattern
ZIF-8 + 1/8 Sodium formate	1/8 The amount in the paper	ZIF particles didn't settle fully Cube shaped particles of ~150nm in size. Very monodisperse. XRD shows ZIF-8 pattern
ZIF-8 + 1/3 Sodium formate	1/3 The amount in the paper	ZIF particles settled out of MeOH Quite polydisperse. Average particle size about 500nm XRD shows ZIF-8 pattern
ZIF-8 +0 sodium formate	0 sodium formate, followed paper method for a control	~100nm XRD shows ZIF-8 pattern
ZIF-8 + 1-MeIM	Following paper method[35] Molar ratio Zn:2MeIM:N1-MeIM 1:4:4 In MeOH (100ml), 24hrs, room temp	~2µm very monodisperse, very nice particle morphology. XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 +1/2 1-MeIM	½ The amount in the paper	~1µm, nicely monodisperse XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 + ¼ 1-MeIM	1/4 The amount in the paper	200-500nm Not as nice morphology as ½ amount XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 + 1/8 1-MeIM	1/8 The amount in the paper	~150nm quite monodisperse however varying in particle shape. XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 + 1/3 1-MeIM	1/3 The amount in the paper	400-600nm, varying shapes XRD shows nice sharp peaks.

The first thing that was clearly noticeable was that the particles had already settled to the bottom of the flask due to the absence of stirring and they also came out of the solution much more easily during centrifuging. As well as this they were redispersed in the MeOH for washing

much more readily. This indicated straight away that the particles produced are larger than those previously made. The XRD pattern of the particles showed that pure-phase ZIF-8 had been prepared when compared to the pattern of known ZIF-8 samples (***Figure 15***). These particles were imaged with SEM imaging and were seen to be of ~1.5 µm in diameter and have very well defined particle morphologies (***Figure 16a***). They also look to be reasonably monodisperse as can be seen in ***Figure 16b***, where there is not much variation in the particle sizes of the sample seen.

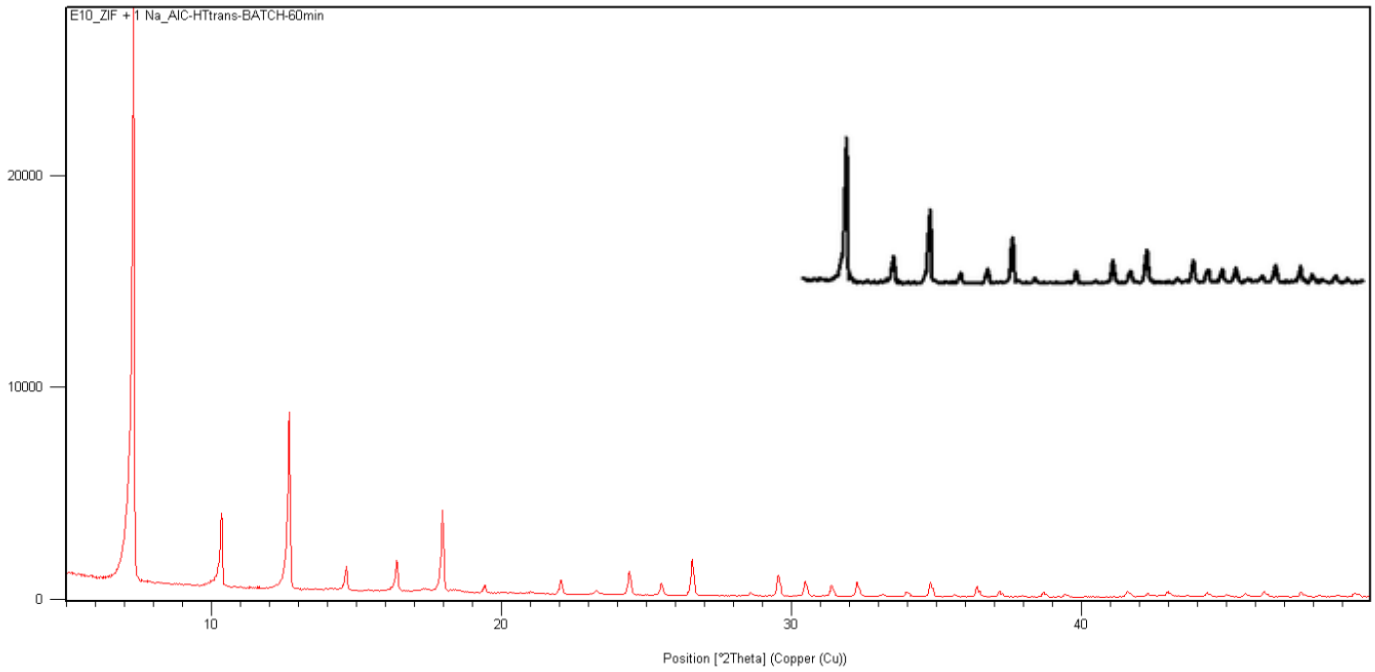


Figure 15- *XRD pattern of ZIF-8 prepared in the presence of sodium formate as the modulating ligand*

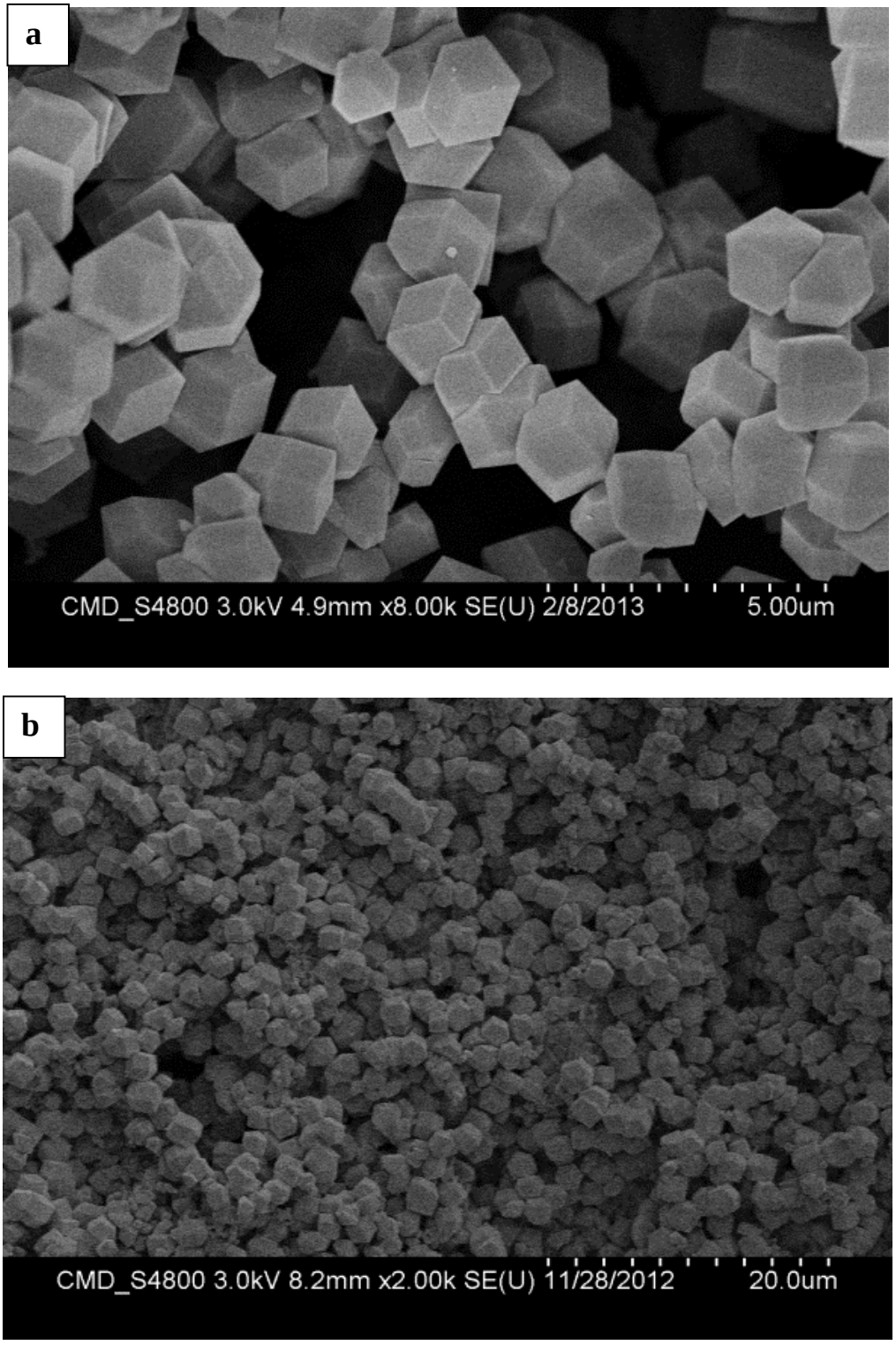


Figure 16- ZIF-8 prepared using the method by Cravillon et al, in the presence of sodium formate (9.88mmol). ~1.5µm particle size. (1:4:4:1000) - reasonably monodisperse.

These particles are much more suitable for our purposes than those made in the initial attempt, as they are much larger than those previously produced and have much more well defined particle morphologies. The ability to control the particle size by adding an auxiliary ligand is very interesting, and it was decided that this would be investigated further to try to manipulate the particles to get ZIF-8 particles of sizes and shapes that were in the range that had been decided (100 nm- 2 μm). The fact that these particles are much larger will make them much more easily visible in the polymer structures when carrying them forward into the composite study, but they may be slightly too large causing them to fall out of suspension and to give a non-homogenous system.

A study was carried out into the possible control of particle size by varying the auxiliary ligand and its concentration. The amount of sodium formate used in the reaction mixture was reduced to produce 6 different concentrations, the amount used in the paper being multiplied by 1, ½, 1/3, ¼, 1/8 and 0 to give 6 different reaction conditions.

The ½ concentration condition produced polydisperse particles of between 500 nm and 1 μm in diameter as can be seen in ***Figure 17***.

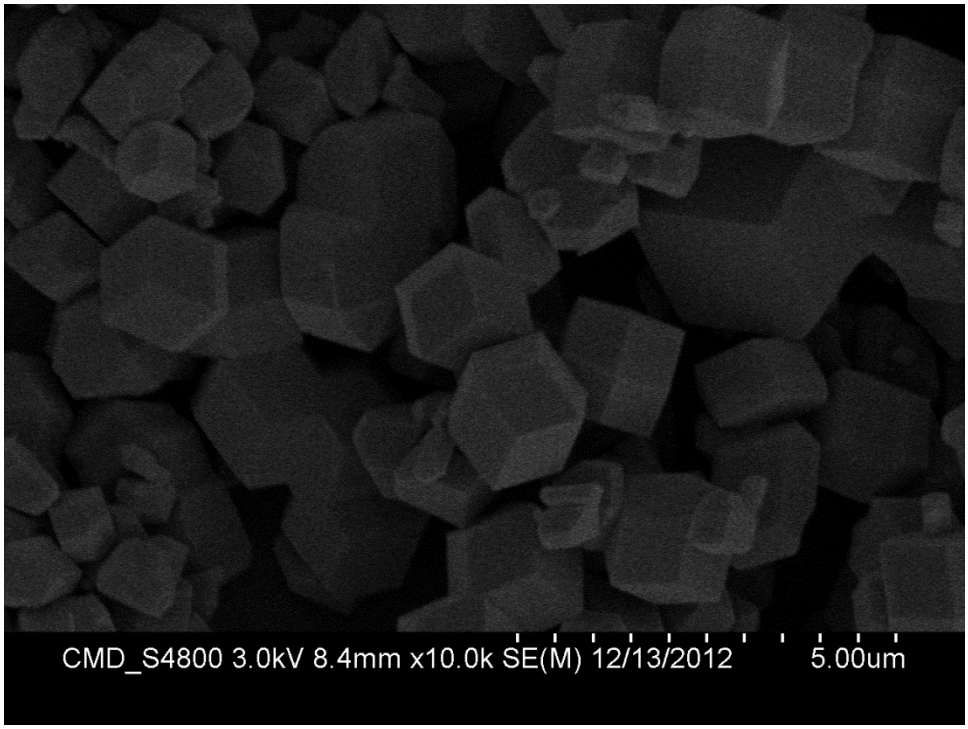


Figure 17- ZIF-8 + 1/2 Sodium formate in MeOH.

These particles are approximately half the size of those prepared with the full amount of sodium formate, as defined by the paper by Cravillon et al, although they are quite polydisperse. They do however still have a very regular particle morphology and therefore it was decided to try 1/3 sodium formate in order to try to keep the particle size reasonably large whilst trying to gain more monodispersity.

The ZIF-8 particles prepared in 1/3 sodium formate again were quite polydisperse particles and this time there was also a number of different particle morphologies. The average particle size was ~500nm so the trend looks to be that the less auxiliary ligand added to the reaction mixture, the smaller the ZIF-8 particles produced (***Figure 18***).

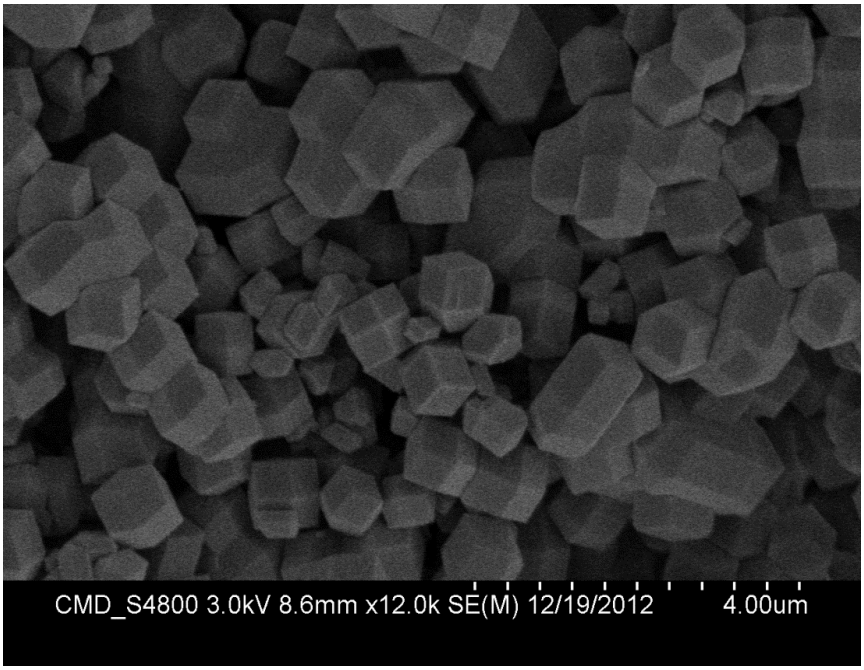


Figure 18- ZIF-8 + 1/3 Sodium formate in MeOH.

Although there are particles produced which look reasonably different, as well as particles which appear to have aggregated, the XRD pattern still shows that pure-phase ZIF-8 has been produced, with very sharp peaks showing a highly crystalline product (***Figure 19***).

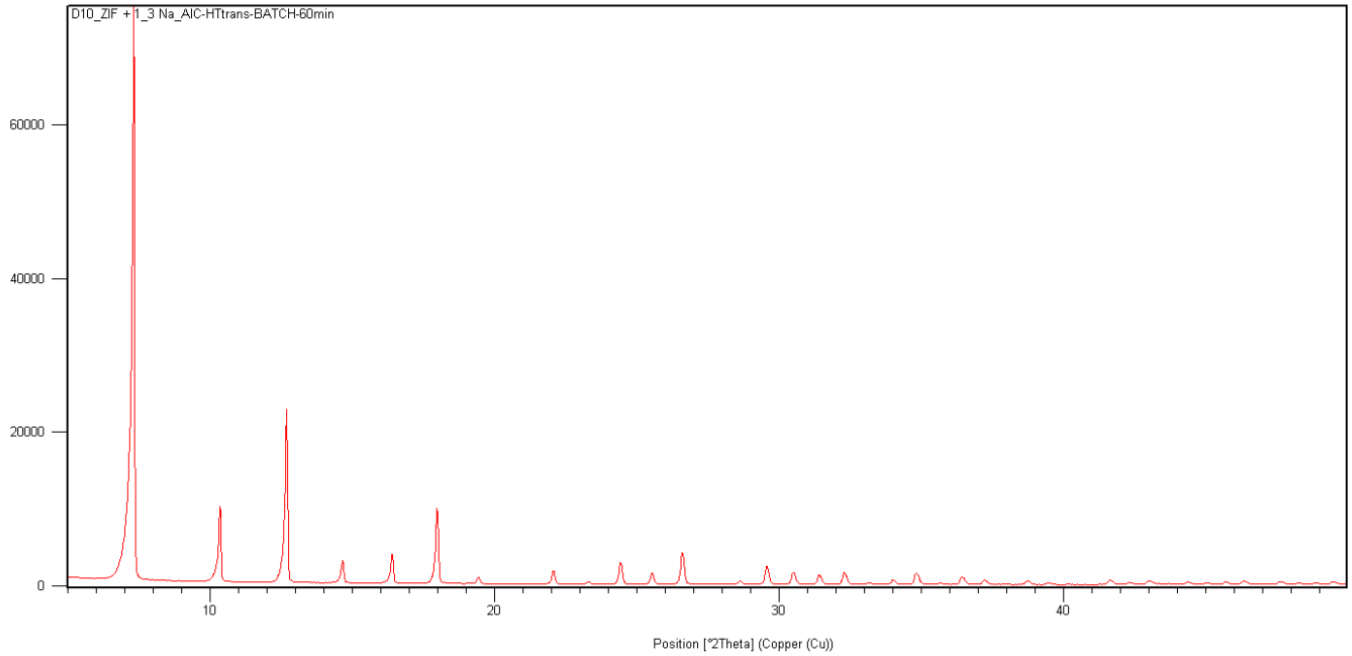


Figure 19- XRD pattern of ZIF-8 +1/3 Sodium formate in MeOH.

The ¼ amount of sodium formate produced particles which had a significantly different morphology to the ZIF-8 produced at higher concentrations of sodium formate. These particles were mostly cubes and had an average particle size of 300nm. These were a lot more monodisperse although there were some big cubes, but these could just be several of the smaller cubes aggregated together. If these particles are single crystals then there is the possibility of trying to improve the procedure by faster mixing of the two solutions, possibly by using an automated method, and less stirring at the start of the reaction to ensure that nucleation of the particles happens simultaneously. The cube shaped ZIF-8 particles can be seen in ***Figure 20.***

The particles formed in the condition with 1/8 sodium formate were of ~150 nm in diameter and were very monodisperse. This condition, like that with ¼ sodium formate, produced ZIF-8 particles with cube-like morphologies. These particles may be too small however, although they do produce nice SEM images unlike the particles formed in the initial experiment with 1:8 ratio Zn:2-MeIM.

To compare to the paper method[35], the ZIF-8 were synthesised with the exact same procedure but without any modulating ligand present. This produced particles of ~100 nm which is larger than the paper suggests as they produced particles of~65 nm in diameter.

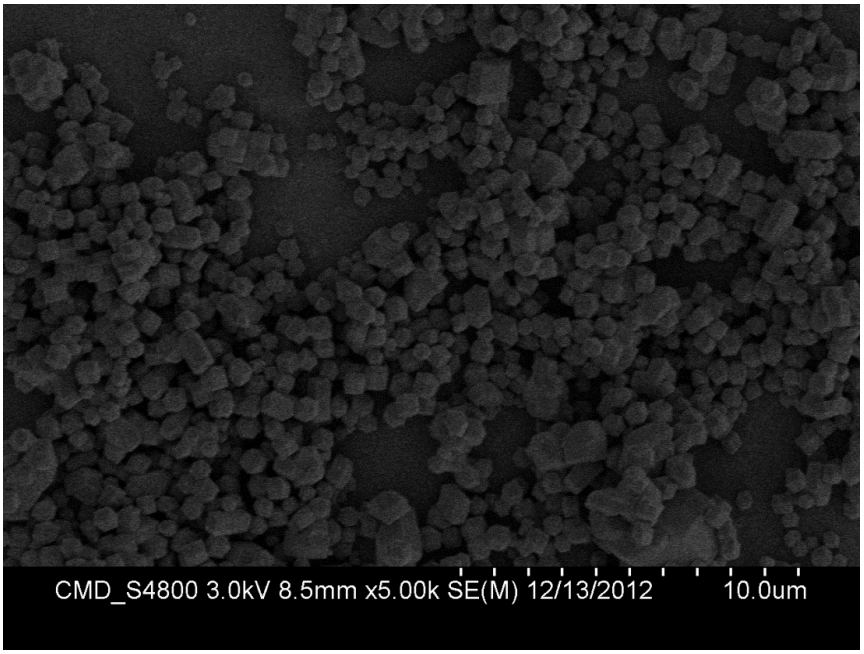


Figure 20- ZIF-8 + 1/4 Sodium formate. These particles have an average particle size of ~300nm.

We also investigated the use of 1-Methyl imidazole (1-MeIM) as the auxiliary ligand. Following the paper[35] method the particles produced were pure-phase ZIF-8 particles that were remarkably monodisperse with very attractive particle morphologies of 2 µm diameter (***Figure 21***). These particles settled out of solution by the end of the 24 hours and were very easy to separate from the MeOH in the centrifuge.

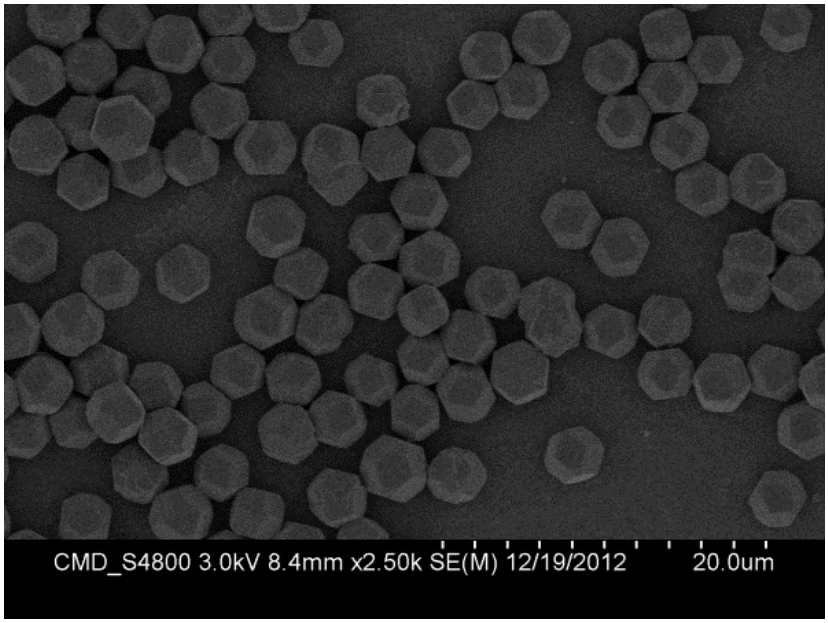


Figure 21*- ZIF-8 + 1-MeIM (9.87 mmol). Very monodisperse particles of 2 µm in diameter.*

The same conditions were investigated for the 1-MeIM auxiliary ligand as were explored for the sodium formate reaction conditions. The amount of 1-MeIM was reduced each time and the particles produced were characterized by XRD and SEM. The most monodisperse particles were produced from the ½ 1-MeIM condition, where particles of 1 µm were formed, which can be seen in ***Figure 22***.

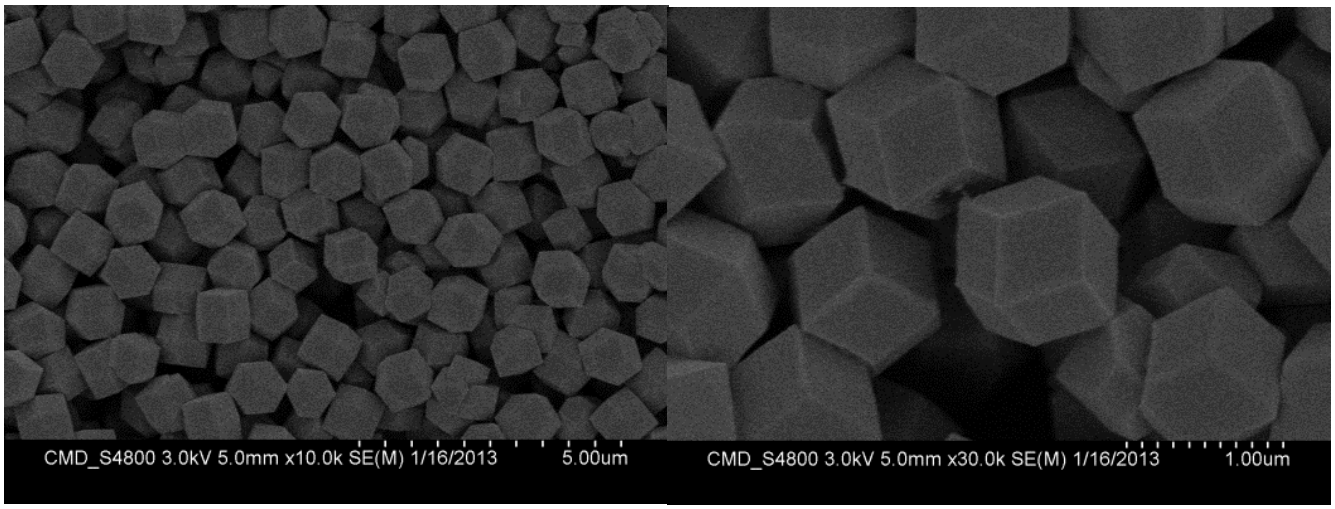


Figure 22*-ZIF-8 +1/2 1-MeIM in MeOH. Very nicely monodisperse particles of 1 µm in diameter. Very well-defined particle morphologies.*

Using the 1-MeIM auxiliary ligand gave the same trend as with the sodium formate, with the average particle size reducing from 2 µm for the full amount of 1-MeIM, through 1 µm (1/2 1-MeIM), 750 nm (1/3 1-MeIM), 400nm (1/4 1-MeIm) and finally 150nm for (1/8 1-MeIM). The average particle size was calculated using a measuring software and taking a measurement of 20 particles. These particles were much more monodisperse however than their counterparts using sodium formate.

The trend in the two sets of reaction conditions can be seen in ***Figure 23***, which shows that the particle size decreases as the concentration of auxiliary ligand decreases in quite a smooth systematic way. The control in the 1-MeIm series however, will be more precise as there are larger size differences and the particles are a lot more monodisperse with more uniform particle sizes. These particles are much more attractive than those produced using sodium formate, for carrying forward for further processing with the aim to prepare some composite materials.

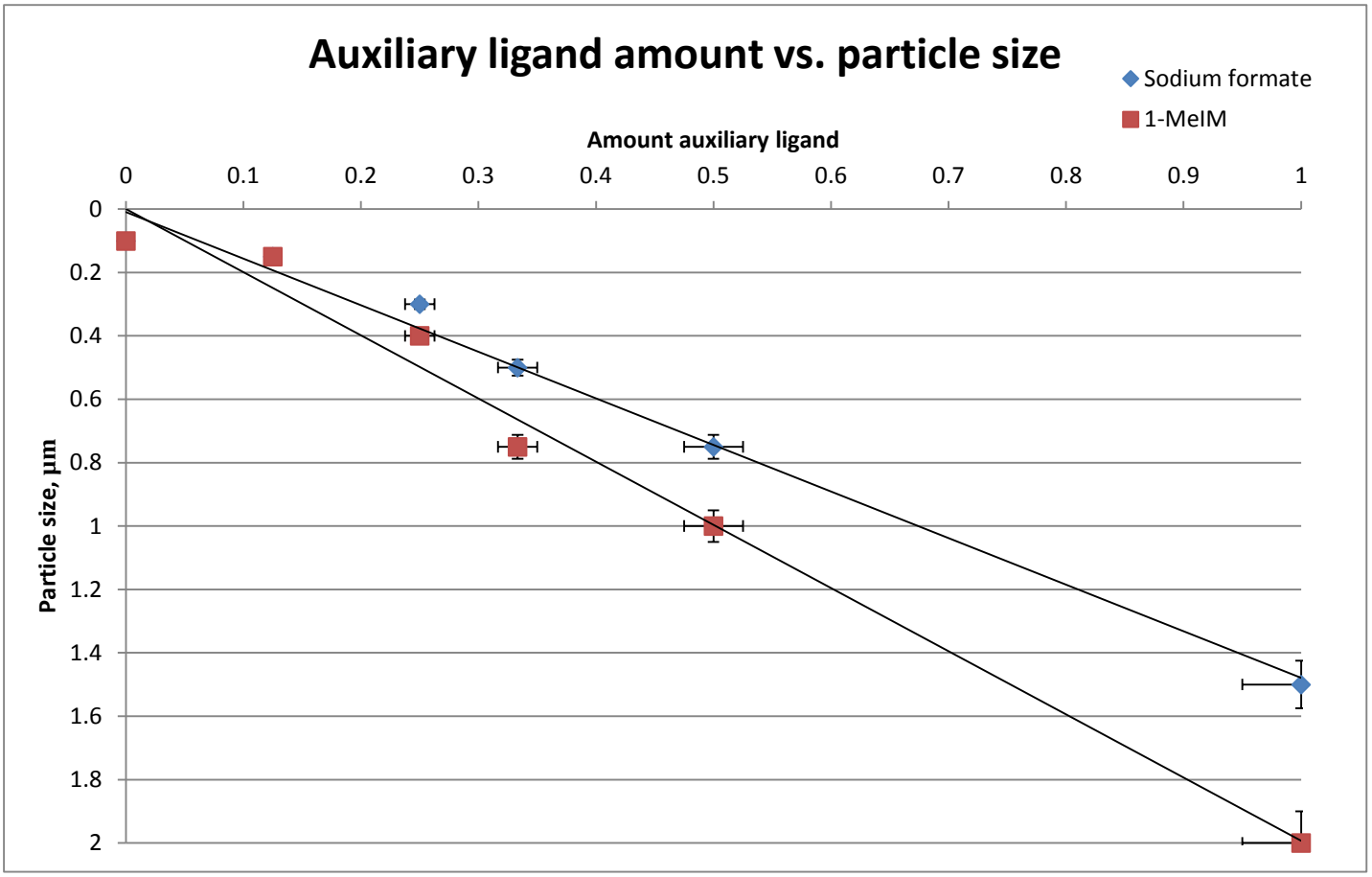


Figure 23 *-Graph to show trend in particle size with changing concentration of auxiliary ligand.*

From these findings we see that the lower the ratio of Zn:2-MeIM and also the addition of the modulating ligand have changed the particle size. These findings could be explained by several reasons.

The increase in size of the crystals is attributed to the addition of the auxiliary ligands. One possible reason for this size increase is that the auxiliary ligand is acting in competition to the bridging 2-MeIM ligand in equilibrium, hence stopping the 2-MeIM from coordinating to the Zn ions. This is due to the extremely labile nature of Zn^{2+} complexes and their ability to form complexes with many different ligands. So the Zn^{2+} ions are not available for coordination with the 2-MeIM or they are coordinated to both 2-MeIM and the auxiliary ligand. This means that the ZIF-8 framework grows much more slowly resulting in a larger crystal size. As the concentration of these auxiliary, competing ligands is reduced, the nucleation and crystal growth rates speed up resulting in smaller particles ultimately forming.

The fact that the ZIF-8 particles formed in the presence of 1-MeIM are larger than those prepared in the corresponding sodium formate conditions is due to the fact that 1-MeIM coordinates more strongly to Zn than does sodium formate. This means that the nucleation rate of the ZIF-8 particles is slowed down even further in the cases where 1-MeIM is used than they are when sodium formate is used, making the resulting particles even bigger. This has been seen before when ligands of apparent low basicity are used as modulating ligands. They affect the crystal growth but they are most important in the nucleation rates, slowing them down and this has the most marked effect.[26, 35, 62, 63]

The original method attempted used a ratio of 1:8 Zn:2-MeIM, and the decrease in the ratio of Zn:2-MeIM to 1:4 has caused a slight increase in the particle size, from 50 nm to 100 nm. In comparison to the method attempted by Venna et al[62], the particle size has not changed. This is a very positive result as there have been a lot of reports stating that there must be a large excess of 2-MeIM in comparison to the Zn to give successful particles. Not only does this method allow the successful preparation of ZIF-8, it also increases the particle size in comparison to those previous methods. In this method there was only a 1:4 ratio of Zn:2-MeIM and are therefore it is using less reagent. This is especially attractive if the reaction is to be scaled up for industrial scale processing.

This procedure, using an excess of 2-MeIM and varying the concentration of auxiliary ligand has allowed the size of the ZIF-8 crystals to be controlled from nano- to microscale and also

shows at a certain level, reasons why this may be occurring. The competition between the auxiliary ligand and the 2-MeIM results in the slower nucleation and crystal growth as they coordinate with the Zn ions in an equilibrium. By controlling and varying the amount of reagents used, the size of the particles produced can be tuned quite precisely. This will allow appropriate ZIF-8 particles to be selected based on their particle sizes and shapes which endow them with certain properties and hence make them more suitable for their chosen application.

Another thing which was desired to do was to redisperse the ZIF-8 particles in water to allow for further processing of the particles. This is because, using this procedure a large amount of MeOH is used which is unfavourable for large scale production of ZIF-8. As well as this, for composite preparation aqueous solutions of polymer are used so the desire is to be able to disperse ZIF-8 in this aqueous polymer solution. When the ZIF-8 that had been prepared in MeOH was redispersed in water it would no longer come out of the solution when centrifuged using the slower centrifuge. The centrifuging was being carried out to ensure no more MeOH was present. This centrifuge has a maximum rpm of 5000. Initially, it was thought that the reason that the ZIF-8 would not separate from the water was because it has a more similar density and therefore needs faster speeds of rpm to separate it from water. So the solutions were transferred to the smaller and faster centrifuge to attempt to separate the particles from the solution. A speed of 10,000 rpm was used for 20 minutes with no particles settling at the bottom of the tube. The rpm was turned up higher, to 12,000 rpm and this was left for 15 minutes. After this time there was some settling at the bottom of the tube. However, there was an unusual observation. The ZIF-8 seemed to form an aggregate which, when centrifuged, moved to the top of the tube, above the water. This was thought to be because of the presence of MeOH in the pores, so the solution was left overnight to allow for the full diffusion of the MeOH out of the ZIF-8 pores. The next day this was centrifuged again at 12,000rpm for 30 minutes and but the aggregate was still present and again, moved to the top of the tube. It was then considered that perhaps the synthetic method used in MeOH did not make ZIF-8 that was stable in other solvents and that the ZIF-8 may be breaking down. This however would be very different to previous reports in which ZIF-8 has been found to be stable in boiling solvent for extended periods of time.[25, 26, 64] XRD measurements and SEM images were taken to further investigate this unusual observation. The particles investigated were ZIF-8 prepared in the presence of sodium formate following the exact procedure in the paper.[35] The images in ***Figure***

24 show the particles before and after the formation of the aggregate, and there doesn't seem to be any difference in the particle morphology.

There are some very small particles on the surface of the large ZIF-8 crystals, which are probably smaller ZIF-8 particles aggregated on the surface. This could begin to explain what is happening. The reaction may be being stimulated to start again by the fast spinning and the presence of a new solvent. There must be some residual starting materials present which are causing the formation of small, nucleating, ZIF-8 particles which could be reducing the density of the aggregates in solution.

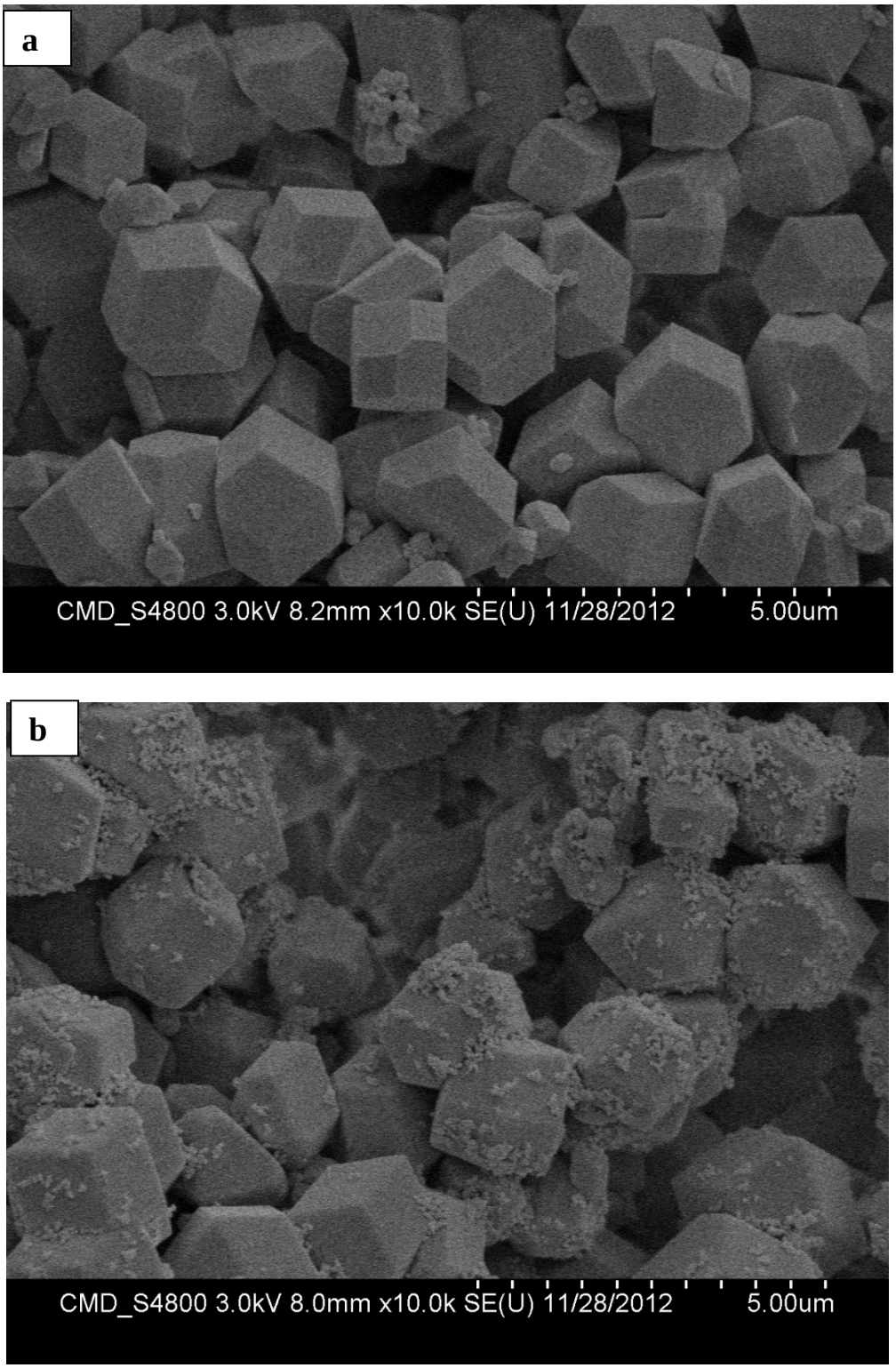


Figure 24*-(a)- ZIF-8 prepared in the presence of sodium formate. (b)- The same particles but after they have been redispersed in water.*

The XRD pattern of the precipitate also showed that the particles were still ZIF-8. Although there are some small peaks present that are not in the XRD pattern for ZIF-8.

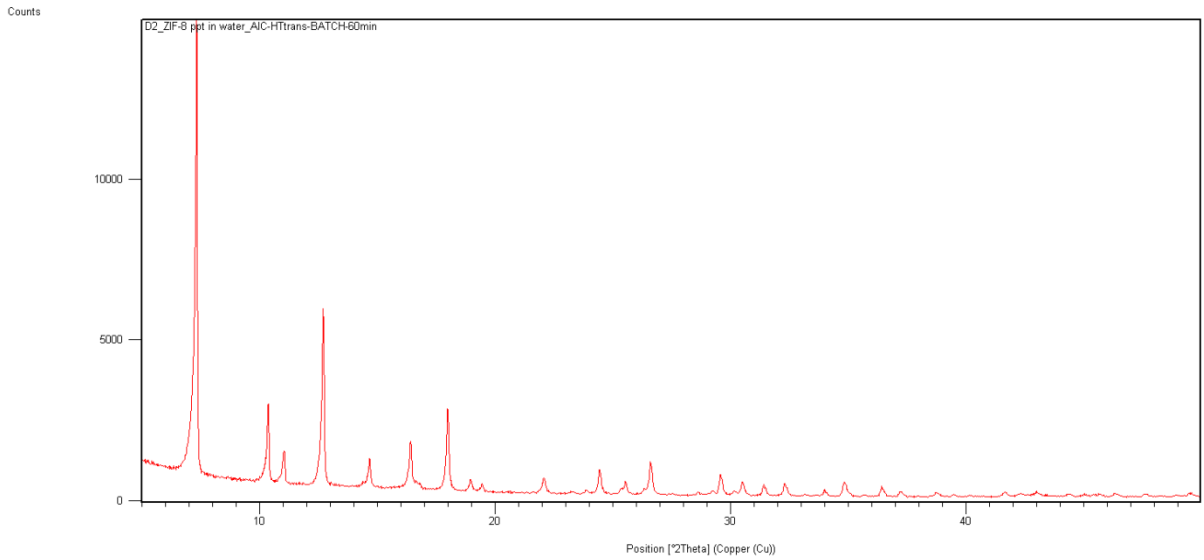


***Figure 25**- XRD pattern of the aggregates formed when redispersing ZIF-8 formed in methanol into water*

There is obviously a difficulty in redispersing these particles, prepared in MeOH, in water. Therefore the next stage of our investigation will focus on the preparation of ZIF-8 in water to try to avoid this problem.

Conclusion

The preparation of ZIF-8 in methanol has been successful under many different conditions with different temperatures and different concentrations being used as well as preparation in the presence of auxiliary ligands. The use of auxiliary ligands has been successful in allowing the size-control of the ZIF-8 particles synthesised and this can be exploited in order to produce ZIF-8 of specific, chosen sizes for use in applications which have a size-specificity. For the preparation of ZIF-8@polymer composite materials the size range of ZIF-8 chosen to be suitable was between 100nm and 2µm and the particles would have to be relatively monodisperse and have well-defined crystalline structures. The particles which best meet these requirements are the ZIF-8 prepared in the presence of auxiliary ligands, sodium formate and 1-methyl imidazole. The size of these particles can be controlled by altering the concentration of these two auxiliary ligands. Another thing that changes with concentration of these ligands

is the monodispersity of the sample and also the particle morphology. This could also be exploited if particles of a particular morphology were required or desired.

The issues with redispersing the particles in water is possibly due to a secondary nucleation of particles taking place and this will be overcome by attempting the preparation of these size-controllable ZIF-8 particles in water rather than in Methanol.

2.3 Experimental

All materials used were purchased from Sigma Aldrich and required no further purification.

2.3.1 Reaction 1: Synthesis of ZIF-8 (1:8 Zn:2-MeIM)

$Zn(NO_3)_2.6H_2O$ (0.1835g, 0.619mmol) was dissolved in 12.5ml MeOH and to this was added 2-MeIM (0.4058g, 4.949mmol) in 12.5ml MeOH with stirring. This was left stirring for 17 hours at room temperature. The solution turned into a cloudy white suspension. This was then centrifuged and washed 3 times with MeOH and then dried overnight in the vacuum oven. Yield= 57.8mg ZIF-8 (40.7%)

2.3.2 Scaled up Reaction 1 (2.3.1)

The same synthetic procedure was followed as in Reaction **2.3.1** scaling it up by 5 times.

The same synthetic procedure was followed as in Reaction 1 scaling it up by 10 times.

2.3.3 Reaction 2: Synthesis of ZIF-8 (Venna et al)[62]

5:1 ratio Zn:2MeIM

301mg $Zn(NO_3)_2.6H_2O$ (1.01mmol, MW=297.49) was dissolved in 11.3g MeOH and this was added to 659mg 2MeIM (8.03mmol, MW=82.10) in 11.3g MeOH. This was stirred vigorously for 24 hours and then was centrifuged and washed three times with MeOH. The ZIF-8 was dried overnight in the vacuum oven at 75°C.This produced 88.6mg ZIF-8 (38.1% yield).

The same procedure was followed on 2 other samples but including 0.01% CTAB and SDS respectively (2.85mg).These produced 90mg and 93.2mg ZIF-8 respectively (38.7 and 40.1% yield respectively). All of these samples were submitted for SEM imaging.

2.3.4 Reaction 1: ZIF-8 batch synthesis

$Zn(NO_3)_2.6H_2O$ (1.835g, 6.19mmol) was dissolved in 120ml MeOH and to this was added 2-MeIM (4.058g, 0.00449mol) in 120ml MeOH with stirring. This was left stirring for 16 hours at room temperature. The solution turned into a cloudy white suspension.

2.3.4.1 ZIF-8 redispersed in water

25 ml of the batch ZIF-8 was taken and centrifuged, washing three times with MeOH and then a further 3 times with distilled water. The ZIF-8 would not come out of the water using the slower centrifuge. The solution was transferred into smaller centrifuge tubes and centrifuged in the faster centrifuge at 10000rpm for 15 minutes and the ZIF-8 came out.

2.3.5 ZIF-8 synthesis with sodium formate

$Zn(NO_3)_2.6H_2O$ (735.3mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (810.4mg, 0.00987mol) and sodium formate (672.1mg, 0.00988mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension. This was centrifuged at 4000 rpm and washed 6 times with MeOH. This was submitted for SEM imaging.

A small amount of this ZIF-8 + sodium formate in MeOH was taken and centrifuged at 5400 rpm for 2 minutes. The ZIF-8 was redispersed in water. A precipitate formed which went to the top of the tube when centrifuged. This was left overnight to displace the MeOH from the pores and then centrifuged again. The precipitate still moved to the top.

2.3.6 Batch ZIF-8

$Zn(NO_3)_2.6H_2O$ (3.6793g, 0.00124mol) was dissolved in 240ml MeOH and to this was added a solution of 2-MeIM (8.114g, 0.0988mol) in 240ml MeOH with stirring. This was left stirring for 16 hours.

12ml was taken and put into small centrifuge tubes and centrifuged at 5000rpm, washing 4 times with MeOH. The MeOH was removed as much as possible, soaking the remainder up with tissue.1.5ml 2% PVA solution was added to this and this was sonicated for a homogenous

dispersion. This was directionally frozen in liquid nitrogen and placed in the freeze drier for 48 hours. It melted slightly in the freeze drier. This was submitted for SEM imaging.

2.3.7 ZIF-8 synthesis with sodium formate (1/2, ¼, 1/8)

½- $Zn(NO_3)_2.6H_2O$ (733.4mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (808.4mg, 0.00987mol) and sodium formate (339.6mg, 0.00499mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension which then settled to the bottom of the flask.

1/4- $Zn(NO_3)_2.6H_2O$ (735.5mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (810.1mg, 0.00987mol) and sodium formate (164.5mg, 0.002419mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension which then settled to the bottom of the flask.

1/8- $Zn(NO_3)_2.6H_2O$ (738.7mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (812.5mg, 0.00987mol) and sodium formate (84.3mg, 0.00124mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension of which half settled out.

These samples were centrifuged and washed three times with MeOH and then submitted for SEM imaging.

2.3.8 ZIF-8 synthesis with sodium formate (1/3) or 1-MeIM

1/3- $Zn(NO_3)_2.6H_2O$ (736.7mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (812.7mg, 0.00987mol) and sodium formate (222.8mg, 0.003276mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature.

1-MeIM- $Zn(NO_3)_2.6H_2O$ (737.1mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (812.9mg, 0.00987mol) and 1-MeIM (825.2mg, 0.01005mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature.

The two samples were centrifuged and washed three times with MeOH and then they were submitted for SEM imaging and XRD.

2.3.9 ZIF-8 synthesis with sodium formate (1/3, ¼, 1/8, 0)

1/3- $Zn(NO_3)_2.6H_2O$ (738.9mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (814.3mg, 0.00987mol) and sodium formate (224.2mg, 0.00247mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension which then settled to the bottom of the flask. (Yield= 0.106g, 18.6%)

1/4- $Zn(NO_3)_2.6H_2O$ (730.9mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (814.9mg, 0.00987mol) and sodium formate (165mg, 0.002419mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension which then mostly settled to the bottom of the flask. (Yield= 0.236g, 41.6%)

1/8- $Zn(NO_3)_2.6H_2O$ (731.1mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (812.4mg, 0.00987mol) and sodium formate (83.8mg, 0.00124mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension of which settled on the bottom of the flask. (Yield= 0.346g, 60.9%)

0- $Zn(NO_3)_2.6H_2O$ (737.4mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (812.3mg, 0.00987mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. The solution turned into a cloudy white suspension of which settled to the bottom of the flask. (Yield= 0.464g, 81.8%)

These samples were centrifuged and washed 6 times with MeOH.

They were then added to 2ml of 2% PVA solution each and sonicated for 20 minutes to give a homogenous dispersion. They were then directionally frozen in liquid nitrogen and put in the freeze drier for 48 hours. They were then submitted for SEM imaging and XRD and BET analysis.

2.3.10 ZIF-8 synthesis with 1-MeIM (1/2, 1/3, ¼, 1/8)

1/2- $Zn(NO_3)_2.6H_2O$ (734.7mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (812.3mg, 0.00987mol) and 1-MeIM (410.5mg, 0.005mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature.

1/3- $Zn(NO_3)_2.6H_2O$ (730.7mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (813.1mg, 0.00987mol) and 1-MeIM (276.3mg, 0.003365mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature.

1/4- $Zn(NO_3)_2.6H_2O$ (737.6mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (813mg, 0.00987mol) and 1-MeIM (206.1mg, 0.00251mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature.

1/8- $Zn(NO_3)_2.6H_2O$ (732.5mg, 0.00247mol) was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM (813.5mg, 0.00987mol) and 1-MeIM (109.0mg, 0.001328mol) in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature.

These samples were centrifuged and washed 6 times with MeOH and then they were submitted for SEM imaging and XRD.

2.3.11 ZIF-8 preparation +sodium formate in MeOH

Amount of sodium formate	Mass Zn (mg)	Mass 2MeIM (mg)	Mass sodium formate (mg)	Yield (%)
1	730.5	810.6	815.1	6.5
1/2	739.3	814.7	405.0	7.0
1/3	731.1	814.6	230.9	9.9
1/4	736.3	814.0	166.1	16.4
1/8	735.3	815.3	84.6	29.2
0	737.5	814.0	0	31.6

$Zn(NO_3)_2.6H_2O$ was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM and sodium formate in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. These were centrifuged and washed 3 times with MeOH. They were then submitted for SEM and XRD.

2.3.12 ZIF-8 preparation + 1-MeIM

Amount of 1-MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)	Yield (%)
1	738.7	809.5	822.7	8.5
1/2	737.2	811.4	406.2	15.1
1/3	736.5	811.1	258.8	22.3
1/4	735.3	810.1	203.9	23.3
1/8	734.6	818.6	106.9	23.2 (10ml solution lost)
0	734.6	814.2	0	29.6

$Zn(NO_3)_2.6H_2O$ was dissolved in 50ml MeOH and to this was added a solution of 2-MeIM and 1-MeIM in 50ml MeOH with stirring. The stirring was then turned off and the reaction was left for 24 hours at room temperature. These were centrifuged and washed 3 times with MeOH. They were then submitted for SEM and XRD.

Chapter 3- ZIF-8 synthesis in water

3.1 Synthesis of ZIF-8

ZIFs are traditionally made in organic solvents such as dimethylformamide (DMF), diethylformamide (DEF) or methanol, but these solvents are expensive and polluting to the environment. There had, in the past, been no luck synthesising ZIFs in aqueous solvents, as only 1D or non-porous materials were being produced in these procedures. There has however been some significant development in this area in the past 3 years.

Pan et al[26] (2011) reported the room temperature synthesis of ZIF-8 in aqueous conditions with reaction times of only minutes. This is clearly more favourable than the solvothermal approach in terms of reaction time, and energy used as well as safety since the only solvent is water and high temperatures are avoided. They used a large excess of 2-MeIM and water with a ratio of Zn:2-MeIM:water= 1:70:1238. These were dissolved in water and added with stirring at room temperature. The colour change to a milky solution, associated with ZIF-8 formation, happened almost instantly when the mixing occurred and the reactions were left for 5 minutes after which an 80% yield (with respect to zinc) of pure ZIF-8 was achieved.[26]

The broadening of the peaks in the XRD pattern indicates nanocrystals have formed which they confirmed by looking at the SEM and TEM images of the particles formed which showed nano-sized particles with sharp hexagonal faces. The particles were ~85nm in diameter with a small polydispersity index of 0.089 showing a very small range of particle sizes. The ZIF-8 formed was found to have excellent thermal, solvothermal and hydrothermal stabilities. When ZIF-8 is prepared in MeOH it is only stable up to temperatures of 250°C whereas these particles prepared in water were found to be stable at 400°C for up to 5 hours. Their solvothermal stability was tested by placing them in boiling water and boiling MeOH for sustained lengths of time.[26] The particles were stable in boiling water for 5 days and in MeOH for 7 days. This excellent solvothermal stability makes the particles attractive for catalysis, gas adsorption and gas separation. They also investigated changing the Zn:2-MeIM ratio and found that increasing the ratio from 1:70 to 1:200 reduced the particle size from 85 nm to ~50 nm without any change in the particle morphology. The ZIF-8 prepared showed a Type I adsorption isotherm indicating the presence of micropores in the MOFs. This is an excellent example of the fact that ZIF-8 synthesis is possible in water and produces particles with very nice properties and morphologies.

Pan et al[65] also investigated the use of surfactants in their synthesis mixture, using the surfactant cetyltrimethylammonium bromide (CTAB) as a capping agent to control the ZIF-8 crystal size and morphology. Using this technique they managed to produce ZIF-8 with particle sizes that ranged from 100 nm to 4 μm depending on the concentration of CTAB used. The morphologies of the particles also changed from truncated cubic to rhombic dodecahedron. The XRD patterns show that all products are pure-phase ZIF-8 and are highly crystalline. Without the addition of CTAB, just following the method they reported in their previous paper, the particles produced were rhombic dodecahedron in shape with 12 exposed faces, and were ~4 μm in diameter. As the amount of CTAB was gradually increased from 0.0025 wt% through to 0.025 wt%, the morphology changed from truncated rhombic dodecahedron to truncated cubes and the sizes reduced until, at the maximum concentration of CTAB added, they were just 110 nm in diameter. The crystallinity remains the same throughout the different conditions with the surface area and pore volumes remaining approximately the same in all concentrations of CTAB. The particles all showed type I isotherms and therefore all had micropores. They speculate that the addition of CTAB affects the crystallization process and this is what changes the size of the particles. They compared their prepared ZIF-8 to ZIF-8 prepared in MeOH and found that the particle size is significantly bigger, with ZIF-8 in MeOH being ~35 nm. This shows that solvent has a large effect on the crystallization process. The effect of adding CTAB to the reaction mixture wasn't seen in the synthesis of ZIF-8 in MeOH and therefore it seems that it doesn't act as a capping agent when used in organic solvents. However the addition of CTAB in the MeOH synthesis did make the particles more monodisperse.

This again is an interesting study showing the use of aqueous environments in the synthesis of ZIF-8. The use of a surfactant to control the particle size could be taken advantage of when certain sized particles are needed for specific applications.

A paper by Gross et al[66] reported the synthesis of ZIF-8 using aqueous conditions and at room temperature for only 10 minutes. They made both Cobalt (ZIF-67) and Zn (ZIF-8) ZIFs using the addition of a triethylamine (TEA) base which deprotonates the 2-MeIM ligand in this aqueous synthesis, without the unwanted formation of metal hydroxides. Their ZIF-8 is of similar quality to that produced in MeOH but at much closer to stoichiometric Zn:2-MeIM ratios. This is favourable as it will reduce the cost of large-scale synthesis and will make the synthetic procedure much more straightforward. They used a 1:1 molar ratio of 2-MeIM:TEA dissolved in water and then added this to a solution of metal nitrate in an equal amount of water.

The Metal:ligand:TEA:H_2O ratio was varied and was 1:(4-16):(4-16):2255. Their procedure had very good yields with respect to zinc, ranging from 68% to 100%. The XRD patterns agreed with known patterns and their products were found to be pure-phase ZIF-8 with particle sizes of <200 nm. However the particles had a non-uniform shape and size due to the faster growth kinetics in water than in MeOH. They also had lower surface areas than usually reported for ZIF-8 in both MeOH and other water syntheses. This could be due to the TEA being stuck in the pores and thus reducing the surface areas and pore volumes. This method, although giving significant yields and using less reagents, doesn't give as attractive particles as did the method used by Pan et al[26].

There have been several other attempts[67, 68] at synthesis in water, one of which was by Tanaka et al[68] (2012). They used a varying ratio of Zn:2-MeIM:water of 1:4-100:2228 but they kept all other variables constant. They used stirring and left the reaction to run for 24 hours, however the solution did become cloudy immediately, indicating the formation of ZIF-8 straight away. They characterized their samples using XRD, SEM, thermogravimetric analysis (TGA) and N_2 adsorption to determine the surface area. At Zn:2-MeIM ratios below 1:20, the XRD pattern of ZIF-8 was not observed showing that at low concentrations of 2-MeIM, ZIF-8 is not formed. This is a common feature of ZIF-8 synthesis in water, the ratio of Zn:2-MeIM needs to be quite large for the reaction to be successful. At ratio of 1:20 the XRD pattern for ZIF-8 was seen, however the crystallinity was reasonably low. This was seen in the XRD pattern by the very low intensity peaks at the ZIF-8 characteristic sites. But at ratios over this pure-phase ZIF-8 particles were formed with a particle size ranging from 300 nm to 3 μm and the Langmuir surface area was very high at values above 1800 m^2g^{-1}. The XRD patterns showed the characteristic pattern for ZIF-8 with nice sharp peaks. This indicates the high crystallinity of these ZIF-8 particles.

Their particles reduce in size as the ratio of Zn:2-MeIM was increased and the monodispersity of the particles formed also increased. The reduction in size of the particles as more 2-MeIm is present is attributed to the fact that the nucleation density must be very high in the early stages of the synthesis and also the increase in pH as more 2-MeIM is added may affect the particle formation.[68]

They state that in general, the surface areas of ZIF-8 prepared at room temperature are lower than that of ZIF-8 prepared at high temperatures and that this may be due to the presence of guest molecules in the pores.

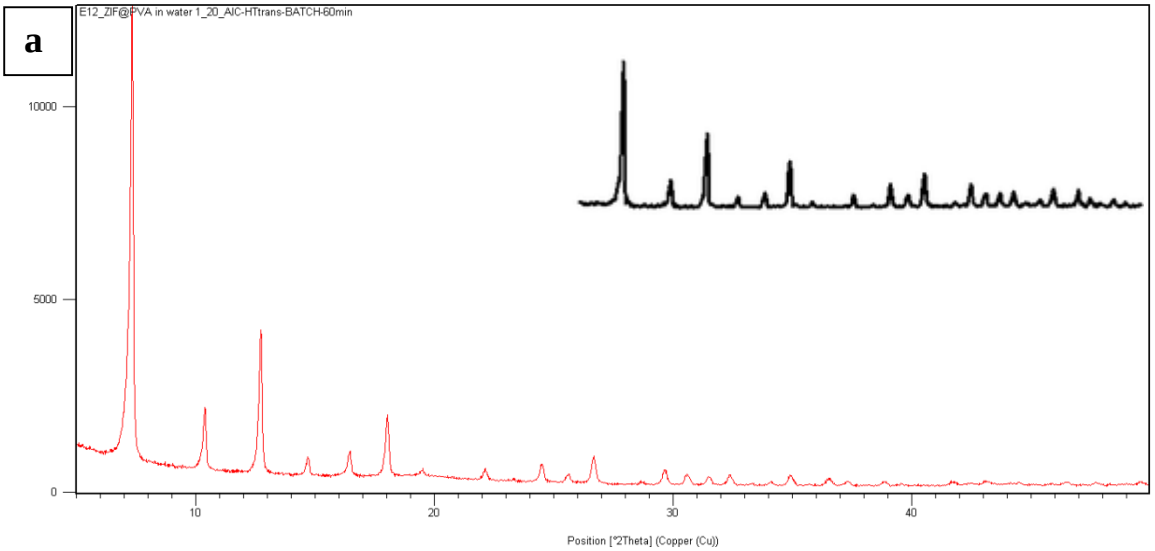
So there has been success in the preparation of ZIF-8 in aqueous media, however the very high ratio of Zn:2-MeIM seems to be required and the particles don't seem to be as crystalline or porous. They also have lower surface areas than their counterparts synthesised in organic solvents. There is however scope for development of these methods and an interest to increase our knowledge of these processes so as to optimize the reaction conditions. The attraction of the syntheses in water such as lower cost, more environmentally friendly, easier syntheses, safer, to name just a few, make this an area of high interest.

The purpose of this chapter is to carry out a systematic study into the synthesis of ZIF-8 in water under several different reaction conditions and to determine the best route to give the most attractive particle properties and morphologies for further application in composite preparation. The chemicals that will be used for this investigation are zinc nitrate hexahydrate, 2-methylimidazole, sodium formate and 1-methyl imidazole.

3.2 Results and Discussion

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) was simply mixed with 2-methyl imidazole (2-MeIM) in a 1:20 ratio and stirred for 24 hours at room temperature in water. The amount of water used in this reaction was a much smaller volume of solvent than was used in the corresponding reactions in methanol, with only 11 ml of water being used whereas in the method by Cravillon et al[35] followed for the size-controlled synthesis in MeOH, 100 ml MeOH was used. This is already a positive over the MeOH reaction, as there will be less waste solvent from this reaction. In this reaction, exactly the same as in the reaction with MeOH, the Zn^{2+} ion centres form a complex with the 2-MeIM linkers and form the well-known sodalite structure to give ZIF-8, as is shown in ***Figure 12*** in Chapter 2.

When this procedure was followed, the particles prepared were found to be pure-phase ZIF-8 from comparison of the XRD pattern (***Figure 26a***) with that of known ZIF-8 patterns, and the particles formed were ~300 nm in diameter. The particles were quite nicely monodisperse although they were very hard to get clear images of and therefore the actual morphologies of the particles could not be identified (***Figure 26b***). As they were not clearly visible, they would not be appropriate for use in composite preparation due to the inability to visualise them in the composite structures.



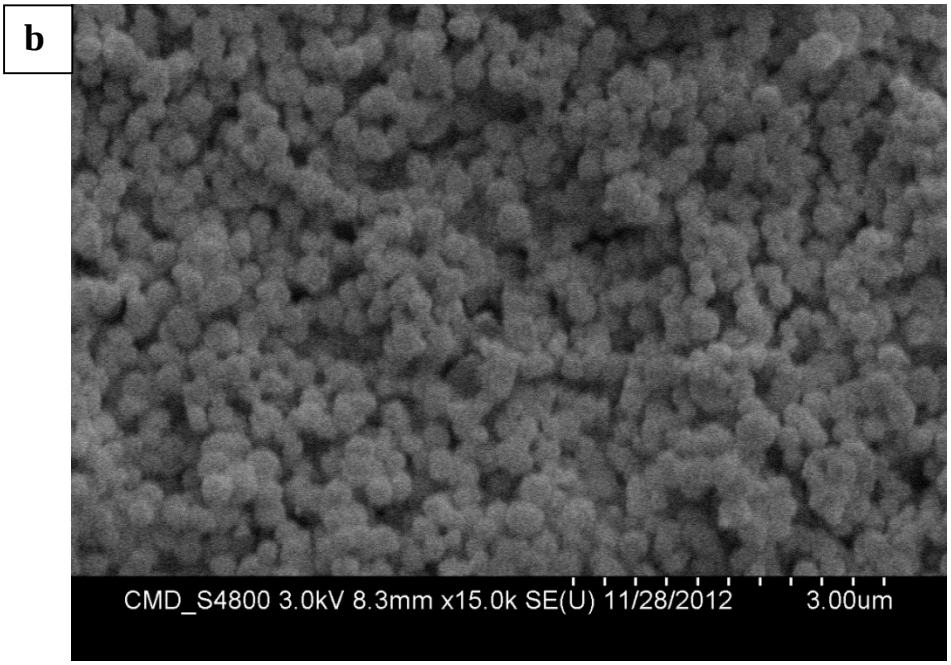


Figure 26*-a) XRD pattern of ZIF-8 in water 1:20 Zn:2-MeIM b) ZIF-8 prepared in water 1:20 Zn:2-MeIm. Particles ~300 nm in diameter.*

To continue with the previous study into the control of the particle size by varying concentrations of reactants, it was decided to increase this ratio of Zn:2-MeIM from 1:20 to 1:40 to try to obtain more well-defined particle shapes. The 2-MeIM needed to be heated

slightly to allow such a large excess to dissolve in only 10ml of water. The particles formed in this reaction were again found to be pure-phase ZIF-8 with particle sizes of ~150 nm and low polydispersity, which can be seen by looking at the SEM image in ***Figure 27***.

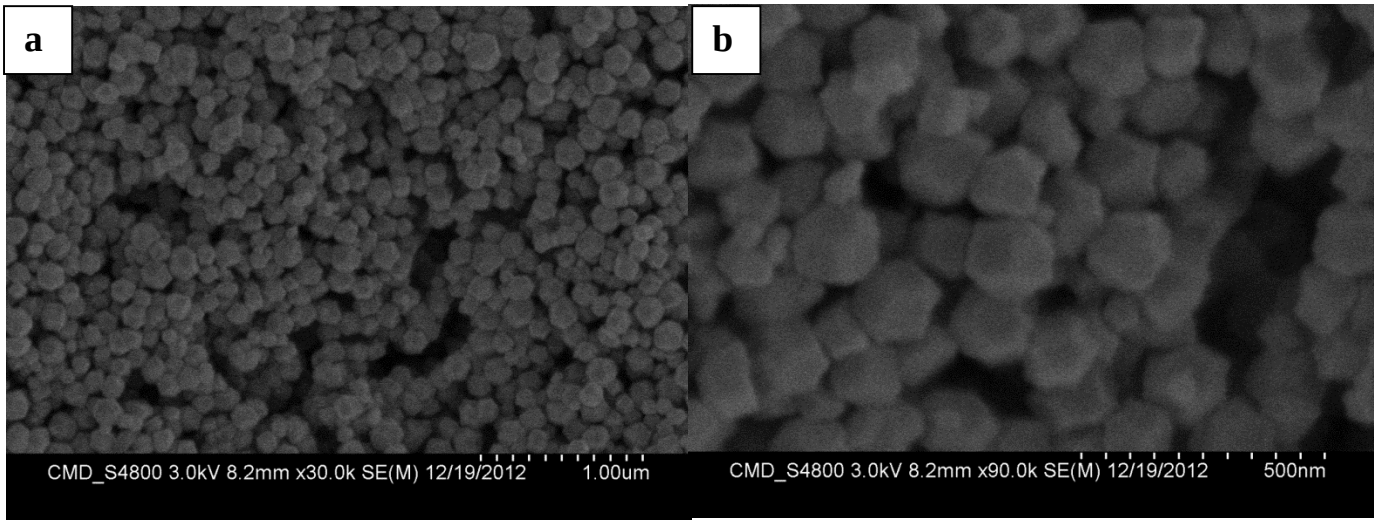


Figure 27*- ZIF-8 prepared in water 1:40 Zn:2-MeIM. Particles are ~150 nm and nicely monodisperse.*

As can be seen by the SEM image in ***Figure 27b***, the particles are more easily visualised than those prepared in 1:20 Zn:2-MeIM and the particle morphologies are starting to become more apparent.

The use of auxiliary ligands in the MeOH synthesis allowed for the preparation of ZIF-8 crystals of controllable particle size and with very attractive, well-defined morphologies. This was especially the case when 1-MeIM was used as the auxiliary ligand. In the two water syntheses tried, the trend seems to be that the reduction in Zn:2-MeIM ratio leads to an increased particle size. So it was decided that these two methods of varying concentration would be used together. The initial test was the room temperature synthesis of ZIF-8 using 1-MeIM as auxiliary ligand varying both the 2-MeIM concentration and the 1-MeIM concentration.

The ratio of Zn:2-MeIM was varied from 1:10, 1:20, 1:30 and 1:40. For each of these 4 conditions there were three different conditions, varying the 1-MeIM ratio each time and keeping the rest of the conditions constant. These conditions shown in the table below, ***Table 2***.

***Table 2**- ZIF-8 synthesis in water + auxiliary ligand 1-MeIM*

Sample	Conditions	Observations
ZIF-8 + 1-MeIM	In water (21ml) 1:10:0 (Zn:2-MeIM:1-MeIM) Room temp 24 hours with stirring	Poorly formed particles- not very crystalline, 500nm-1.5µm. XRD shows ZIF-8 pattern- not a very smooth pattern and peaks are very small
ZIF-8 + 1-MeIM	In water (21ml) 1:10:5 Room temp 24 hours with stirring	Much better defined particle shape ~250 nm-2.75 µm XRD shows ZIF-8 pattern- much sharper peaks than 1:10:0
ZIF-8 + 1-MeIM	In water (21ml) 1:10:10 Room temp 24 hours with stirring	Quite polydisperse, ~250 nm-1 µm XRD pattern shows the characteristic ZIF-8 pattern with the peaks much sharper with the addition of 1-MeIM
ZIF-8 + 1-MeIM	In water (21ml) 1:20:0 Room temp 24 hours with stirring	Not well defined particles and polydisperse, ~100 nm-750 nm XRD shows the characteristic pattern of ZIF-8 but slightly more 'noisy' signal than with 1-MeIM added.
ZIF-8 + 1-MeIM	In water (21ml) 1:20:10 Room temp 24 hours with stirring	Mostly cubes, nicer particles ~100-200 nm XRD pattern shows the characteristic ZIF-8 pattern with the peaks much sharper with the addition of 1-MeIM
ZIF-8 + 1-MeIM	In water (21ml) 1:20:20 Room temp 24 hours with stirring	~350 nm, much more regular particle size compared to 1:20:0 and 1:20:10 XRD pattern shows the characteristic ZIF-8 pattern with the peaks much sharper with the addition of 1-MeIM
ZIF-8 + 1-MeIM	In water (21ml) 1:30:0 Room temp 24 hours with stirring	Very polydisperse, 75-150 nm, not nice particles
ZIF-8 + 1-MeIM	In water (21ml) 1:30:15 Room temp 24 hours with stirring	Mostly cubes, quite monodisperse ~100 nm
ZIF-8 + 1-MeIM	In water (21ml) 1:30:30 Room temp 24 hours with stirring	Quite polydisperse, ~50-275 nm
ZIF-8 + 1-MeIM	In water (21ml) 1:40:0 Room temp 24 hours with stirring	Polydisperse and several morphologies, 100-200 nm
ZIF-8 + 1-MeIM	In water (21ml) 1:40:10 Room temp 24 hours with stirring	Addition of auxiliary ligand improves particle size and shape, ~75-200 nm
ZIF-8 + 1-MeIM	In water (21ml) 1:40:20 Room temp 24 hours with stirring	Addition of auxiliary ligand improves particle size and shape, 75-150 nm

The particles were all characterized by both SEM imaging and XRD diffraction.

In all of the conditions where there was no 1-MeIM added the particles formed were not very crystalline, with poor particle morphologies. This corresponds to what has been reported in previous data, that ZIF-8 needs large excess of 2-MeIM present to be able to form, although we have been able to form ZIF-8 but it isn't of well-defined shape.[26]

As can be seen by looking at ***Figure 28*** which shows the 1:10:X series of conditions, the particle shape becomes much more well-defined and more monodisperse as the concentration of 1-MeIM is slowly increased.

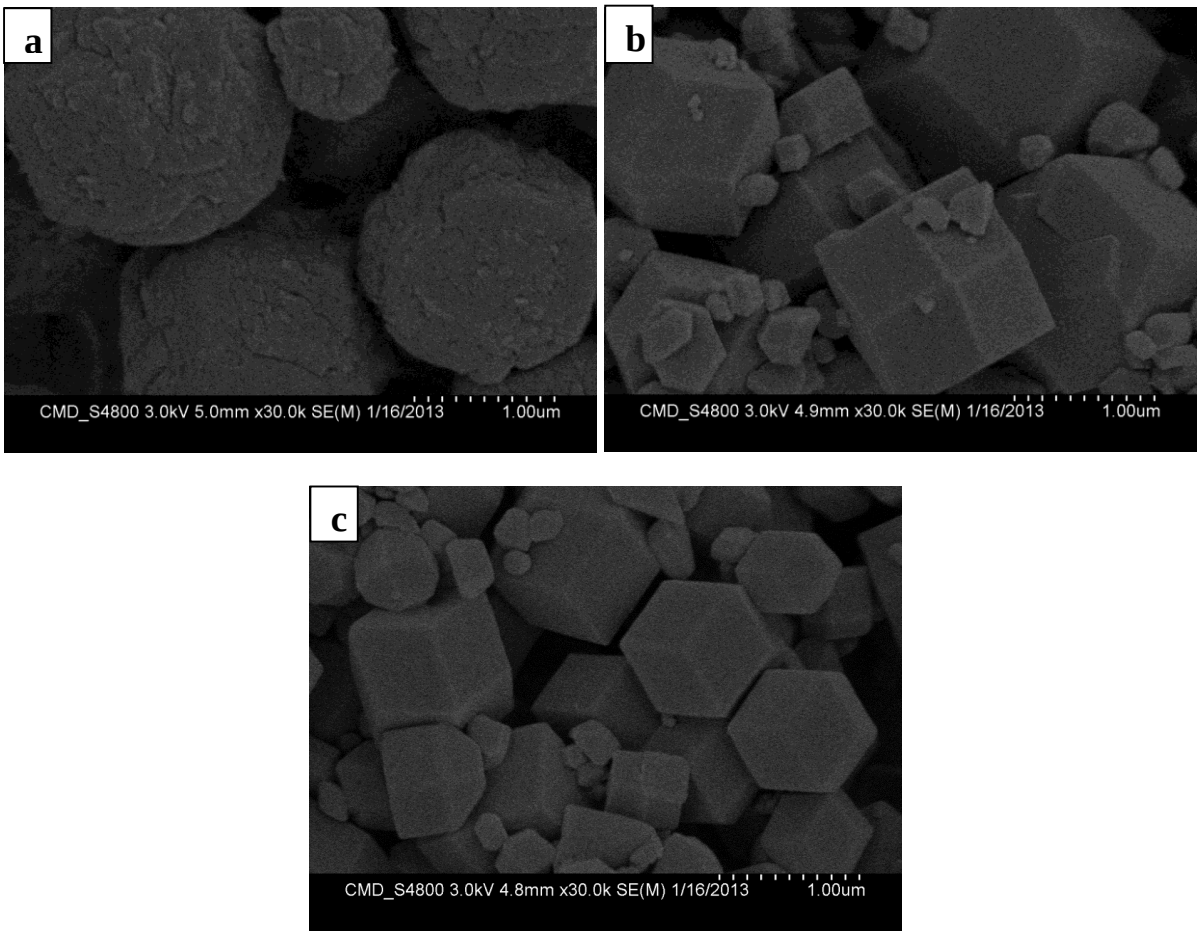


Figure 28*- ZIF-8 +1-MeIM in water: a) 1:10:0, b) 1:10:5, c)1:10:10*

However for the 1:10:X ratio of Zn:2-MeIM :1-MeIM the particles are quite polydisperse in all concentrations of 1-MeIM with the presence of very small nano-particles of ZIF-8 as well as the larger ~1 μm particles formed in all three cases. The ZIF-8 crystals formed in 1:10:0 are quite uncrystalline with their approximately spherical morphology. Although by looking at the XRD pattern (***Figure 29***) for this sample it can be seen that the peaks for ZIF-8 sodalite structure are definitely present with the sharpness of the peaks only slightly reduced.

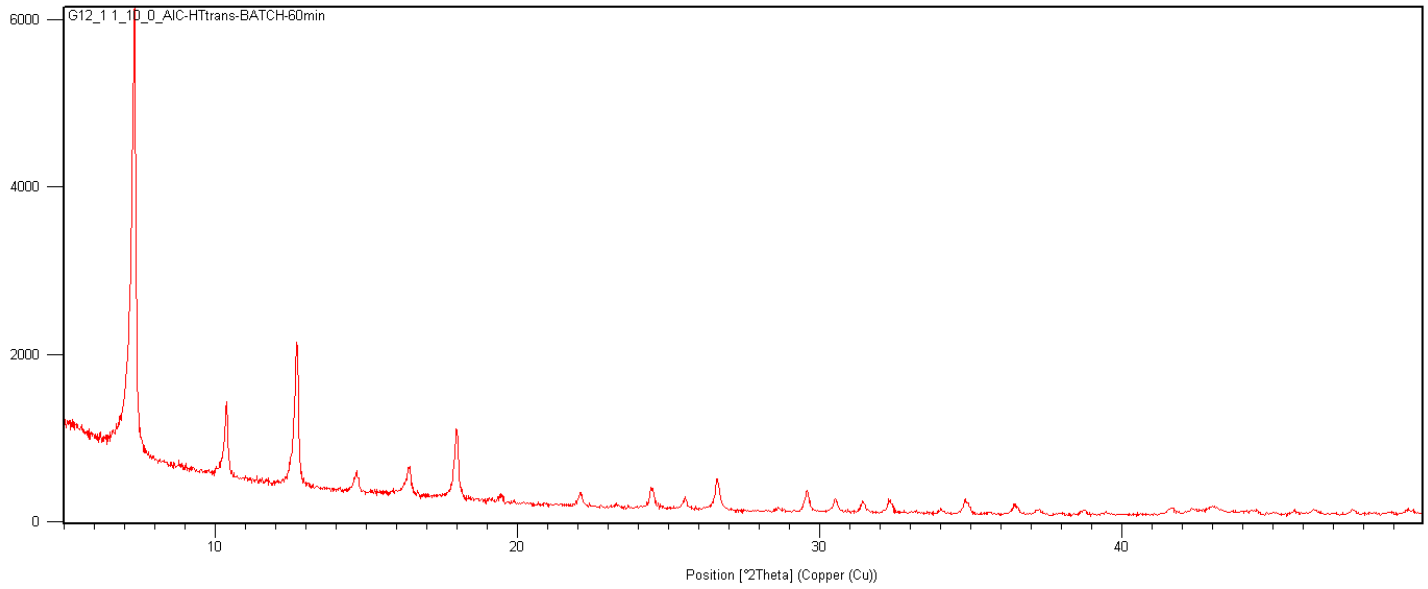


***Figure 29**- XRD pattern for ZIF-8 in water 1:10:0 (Zn:2-MeIM:1-MeIM)*

The 1:20:X series shows the same trend in improved particle morphology with the addition of 1-MeIM. There is however slightly more definition to the shape of the ZIF-8 particles in the 1:20:0 condition, although they are very polydisperse, which can be seen in **Figure 30**. The 1:20:20 condition shows a lot more monodisperse particles, with particles of ~350 nm diameter.

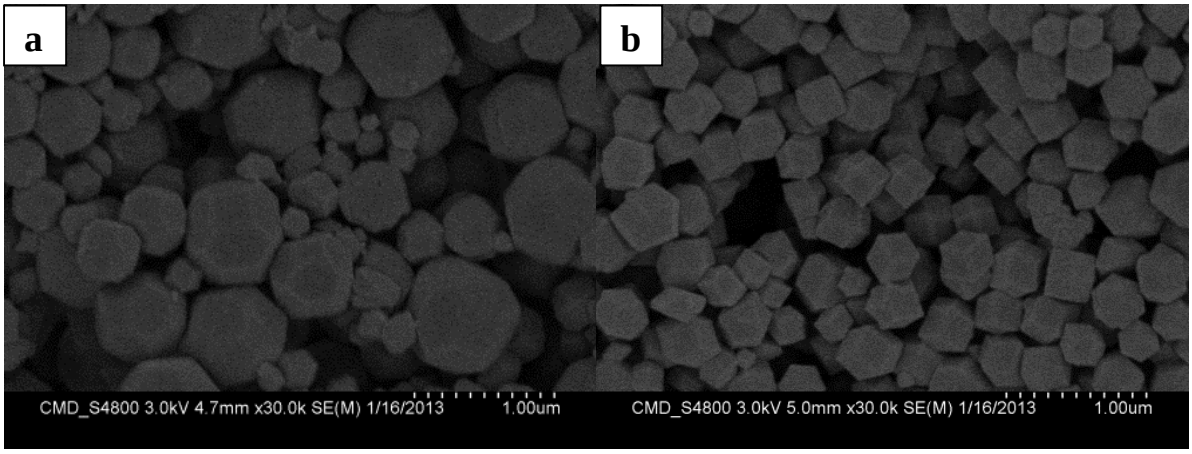


***Figure 30**- ZIF-8 in water + 1-MeIM. A) 1:20:0, B) 1:20:20*

From just looking at these first two sets of conditions, it can start to be seen that there is a different trend in change of particle size with the addition of 1-MeIM in water than there was with the corresponding reactions in methanol. When methanol was used as the solvent the particle size decreased quite dramatically as the concentration of auxiliary ligand was

decreased. This is not the case for these water reactions, as the particle size seems to be relatively similar in all conditions, with the 1-MeIM just improving the particle morphology. There could even be a slight reduction in size as the 1-MeIM concentration is increased, but this will be assessed when we discuss the further reactions. But it is clear that the addition of 1-MeIM is significantly improving the crystallinity and particle morphology of the ZIF-8 crystals, as at lower concentrations of 2-MeIM, without 1-MeIM present the particles are basically spherical with no defined crystal shape, whereas with added 1-MeIM the particles have nice morphologies and start to become more monodisperse.

This trend was also seen for 1:30:X and 1:40:X conditions at room temperature in water.

This improvement in crystallinity and particle morphology with addition of 1-MeIM as an auxiliary ligand is interesting especially when there have been results published that claim a large excess of 2-MeIM is needed to allow successful formation of ZIF-8 particles.[26] We decided to try the synthesis of ZIF-8 at much lower concentrations of 2-MeIM in water in the presence of auxiliary ligand 1-MeIM, to see whether the presence of this additional ligand can allow the formation of ZIF-8 at much lower concentrations of reagents.

Initially we tested this at room temperature and the conditions used can be seen below in ***Table 3***. The concentrations used were 1:1:X, 1:3:X, and 1:6:X with 4 conditions being used for each set of 2-MeIM conditions.

Table 3- *ZIF-8 preparation at low 2-MeIM concentrations + 1-MeIM auxiliary ligand (Room temperature)*

Sample	Conditions	Observations
ZIF-8 + 1-MeIM	In water (20ml) 1:1:0 (Zn:2-MeIM:1-MeIM) Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles XRD pattern shows too many peaks however some of the peaks are in the correct places for ZIF-8
ZIF-8 + 1-MeIM	In water (20ml) 1:1:1 Room temp 24 hours with stirring	**Not ZIF-8-** Starting to become more 3D structures however not the nice structures of ZIF-8 XRD pattern shows too many peaks however some of the peaks are in the correct places for ZIF-8
ZIF-8 + 1-MeIM	In water (20ml) 1:1:10 Room temp 24 hours with stirring	**Not ZIF-8-** Particles are now looking like they're trying to become more crystalline XRD pattern shows too many peaks however pattern is starting to look more similar to the pattern of ZIF-8 with less peaks showing in the pattern.
ZIF-8 + 1-MeIM	In water (20ml) 1:1:20 Room temp 24 hours with stirring	**Not ZIF-8-** Particles are now looking like they're trying to become more crystalline XRD pattern shows too many peaks however pattern is starting to look more similar to the pattern of ZIF-8 with less peaks showing in the pattern.
ZIF-8 + 1-MeIM	In water (20ml) 1:3:0 Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles XRD shows crystalline pattern but not that of ZIF-8- more peaks in pattern- peaks for ZIF-8 do appear to be present amongst the other peaks. Very different pattern to that of 1:1:20
ZIF-8 + 1-MeIM	In water (20ml) 1:3:3 Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles XRD shows same pattern as 1:3:0 but stronger signals, however the single peak on the right has decreased in intensity.
ZIF-8 + 1-MeIM	In water (20ml) 1:3:10 Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles XRD pattern shows too many peaks. Again same signal as 1:3:x with the peaks becoming sharper and the 'noise' of the signal decreasing with increased addition of 1-MeIM.
ZIF-8 + 1-MeIM	In water (20ml) 1:3:20 Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles Again, XRD shows same pattern as 1:3:0 and 1:3:3 however more sharp peaks with less noise, therefore more crystalline.
ZIF-8 + 1-MeIM	In water (20ml) 1:6:0 Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles XRD shows same pattern as 1:3:x, however sharper, more well defined peaks.
ZIF-8 + 1-MeIM	In water (20ml) 1:6:6 Room temp 24 hours with stirring	**Not ZIF-8-** Plate-like particles with some more crystalline XRD shows that the pattern is starting to change as the particles begin to change. The peaks for ZIF8 becoming more pronounced and the number of peaks is diminishing.
ZIF-8 + 1-MeIM	In water (20ml) 1:6:10 Room temp 24 hours with stirring	**Not ZIF-8-** Particles look like becoming more crystalline XRD shows very similar pattern to 1:6:6 however sharper peaks.
ZIF-8 + 1-MeIM	In water (20ml) 1:6:20 Room temp 24 hours with stirring	**Not ZIF-8-** Particles look like becoming more crystalline XRD shows the number of peaks greatly reduced, the pattern of ZIF-8 starting to become recognisable.

The initial observation of these reactions showed that, unlike all previous reactions, where the solutions turned a milky white colour almost immediately on addition of the 2-MeIM solution to the Zn solution, these solutions, after three hours had not changed colour. There was one exception to this, which was the 1:1:X solutions.

The particles were characterized using SEM imaging and XRD measurements.

The SEM images were taken first and they showed some very strange particle morphologies as can be seen in the following images (***Figure 31***).

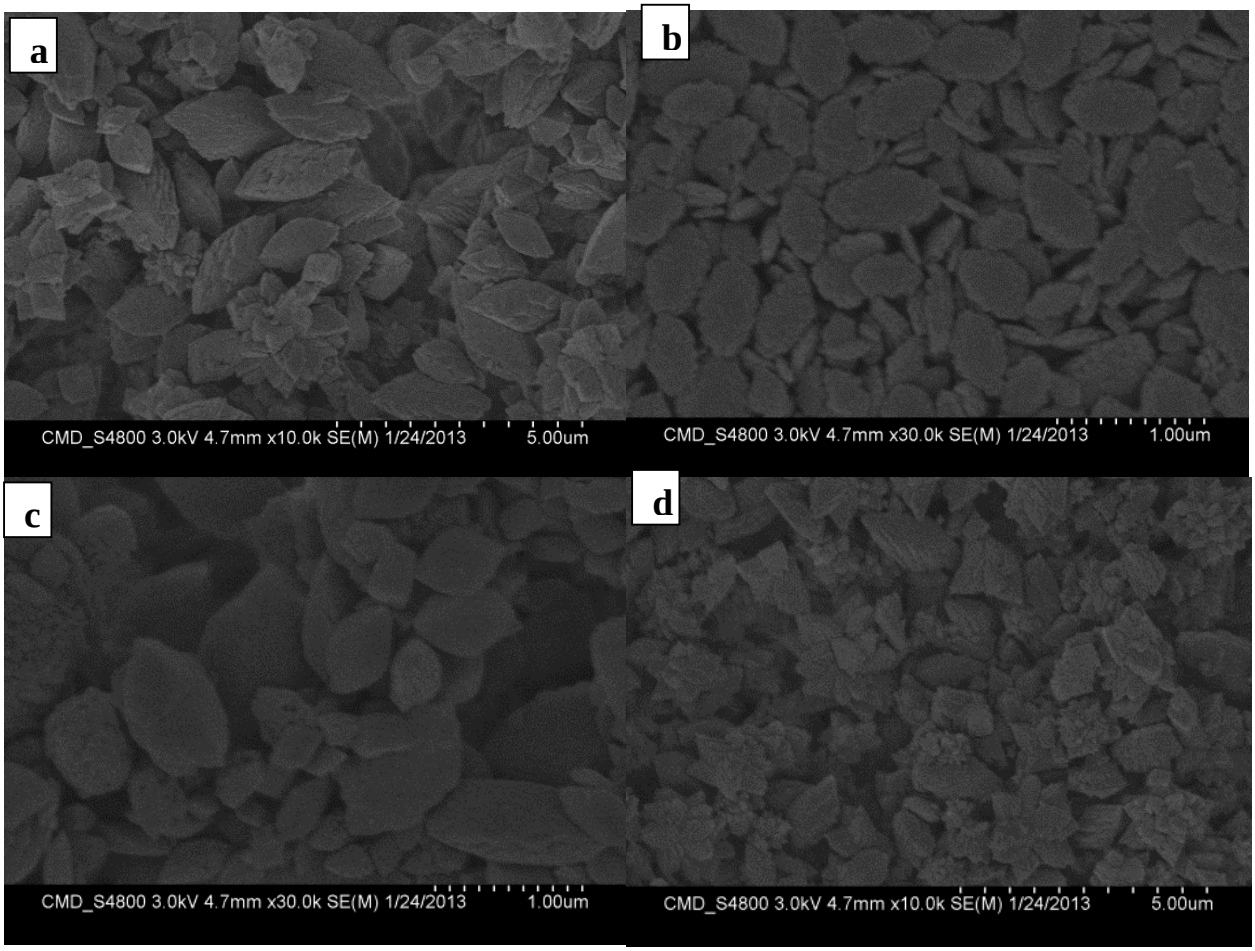


Figure 31*-ZIF-8 +1-MeIM 1:1:X in water at room temperature. a) 1:1:0, b) 1:1:5, c)1:1:10, d)1:1:20*

These particles are quite clearly very different from those previously prepared and this raises the question of whether they are in fact ZIF-8 or whether some other particles have been synthesised. It looks like the particles are becoming more and more crystalline as the amount

of 1-MeIM is increased, and this would support our hypotheses, that the presence of 1-MeIM does help ZIF-8 form at low concentrations of 2-MeIM.

By looking at the XRD patterns of the samples (***Figure 32***), it is clear that pure-phase ZIF-8 has not formed, although there are some peaks forming in the regions where the ZIF-8 peaks should be, showing that the crystals that have formed may be precursor complexes to the ZIF-8 crystal framework, with the similar crystal structure. The additional peaks could be due to differences in the crystal structure, but the particles formed are clearly crystalline as they have well-defined peaks.

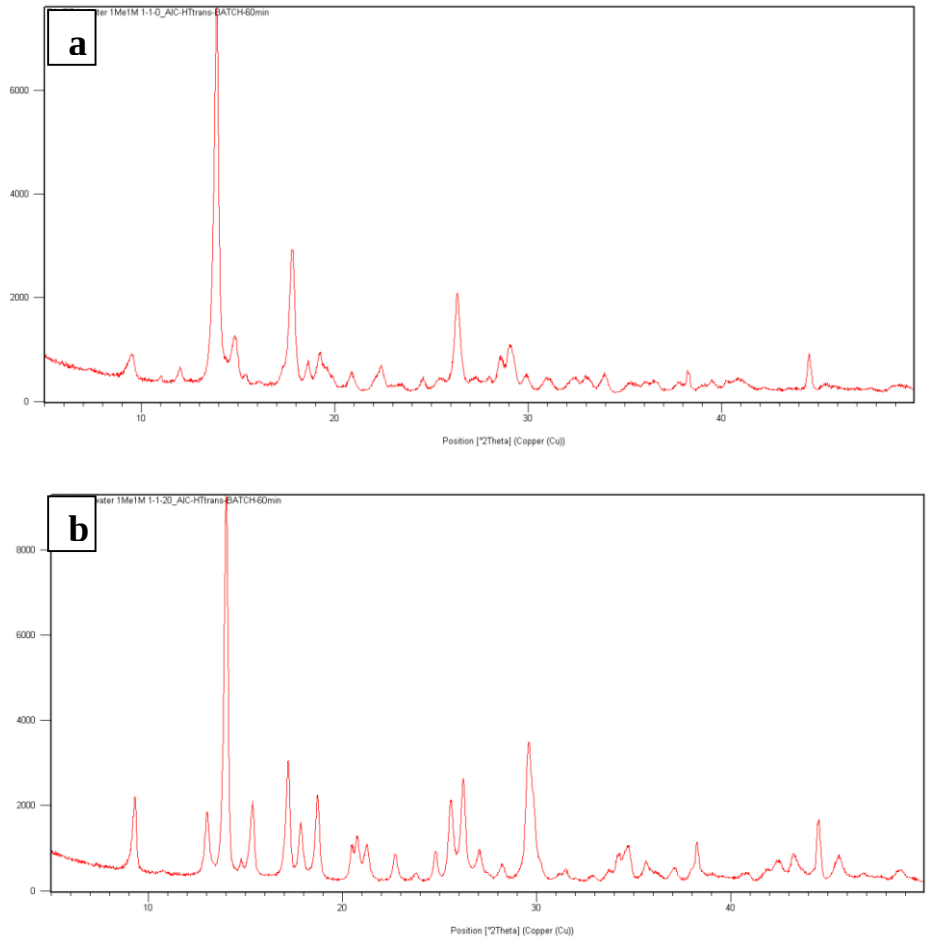


Figure 32- *XRD patterns of "ZIF-8" + 1-MeIM a) 1:1:0 and b) 1:1:20 in water at room temperature.*

The sharper peaks in the 1:1:20 XRD pattern coincides with the more crystalline particles formed which is seen in the SEM images in ***Figure 31***.

This trend was seen in all of these low concentration conditions at room temperature, with the crystal structure becoming more pronounced with the addition of 1-MeIM. The ZIF-8 structure however did not successfully form for any of these conditions.

The 1:3:0 condition produced very unusual “plate-like” particles which can be seen in ***Figure 33***. These particles, as is the case for these other particles which are not ZIF-8, produced an XRD pattern which showed a crystalline structure had formed. These particles were of great interest, and it was decided to investigate whether they would have a high BET surface area, because if they did it wouldn’t matter if they were not successfully formed ZIF-8 particles, they could still be used for similar applications.

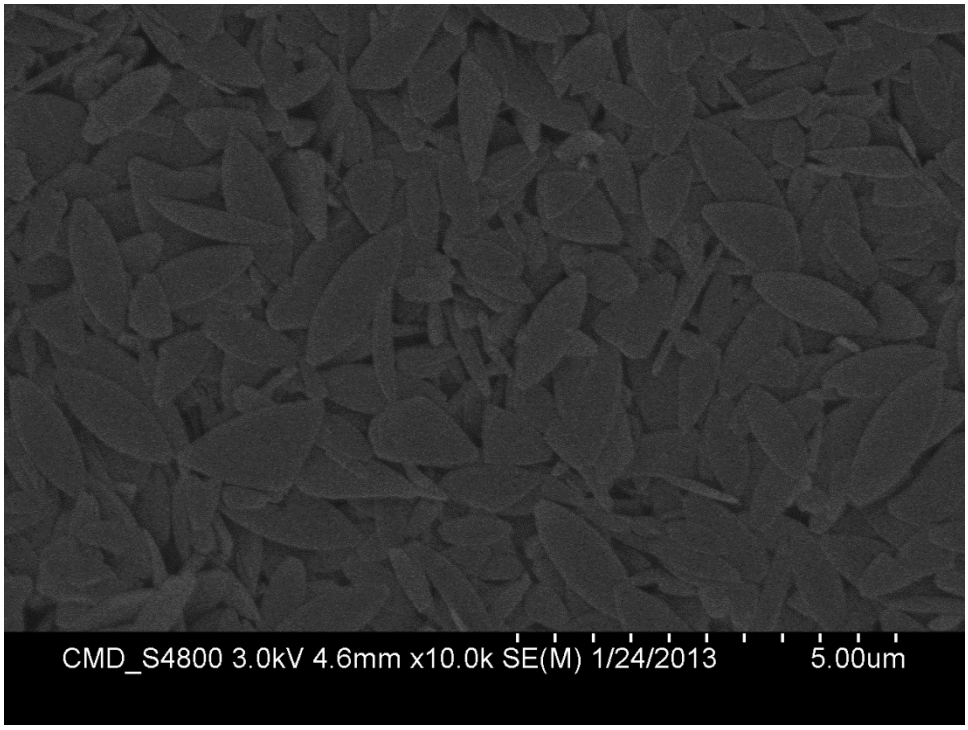


Figure 33*- ZIF-8 +1-MeIM 1:3:0 RT*

The adsorption isotherm shows that the particles are nonporous, and the nitrogen will only be being adsorbed onto the surfaces of the particles. This can be seen below in the adsorption isotherm ***Figure 34***.

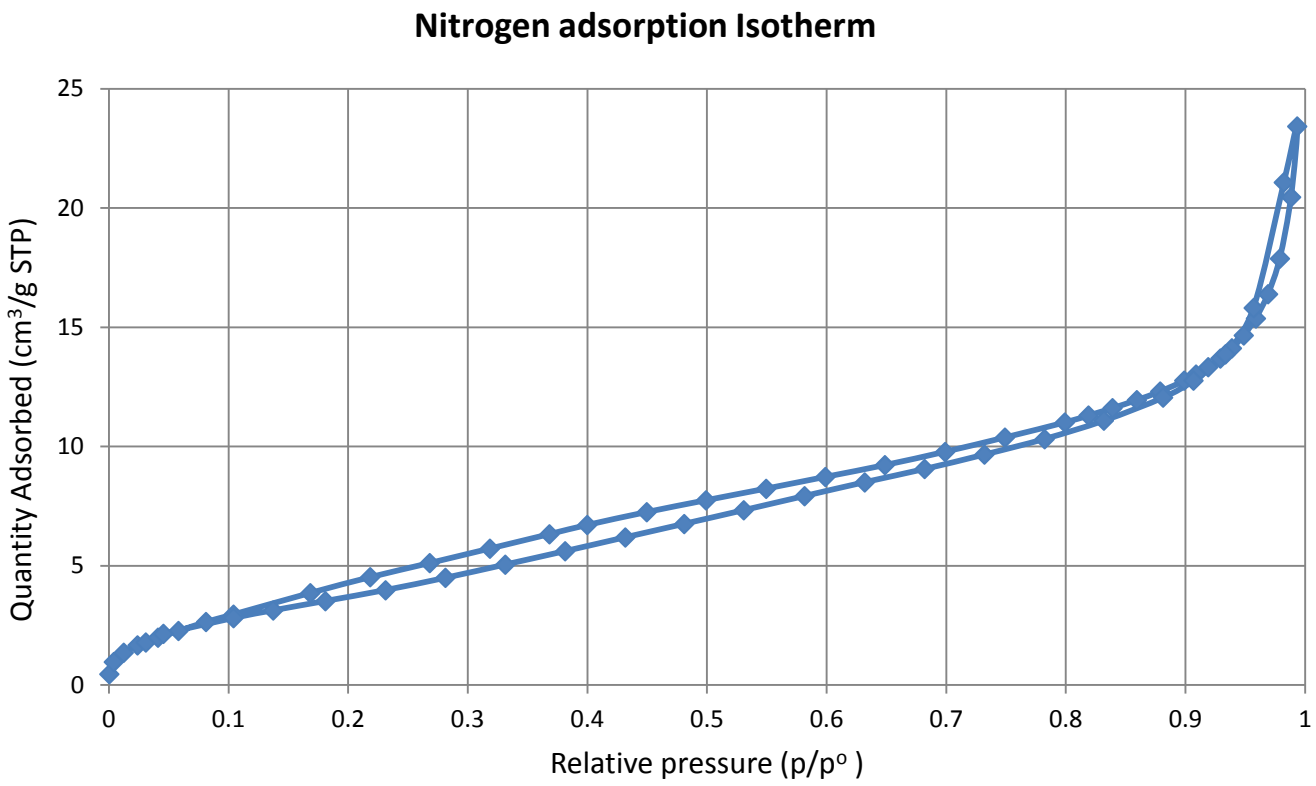


Figure 34- *N_2 adsorption isotherm for the "plate-like" particles 1:3:1 RT*

The BET surface area for these particles was only 10 m^2g^{-1} indicating that they are not porous particles and therefore will not be useful in applications in which ZIF-8 is used.

The closest crystalline product to ZIF-8 was the 1:6:20 condition which gave an XRD pattern which looks remarkably similar to that of ZIF-8, however the peaks are not very well defined and there are still extra peaks in the pattern. This can be seen in ***Figure 35***, where the XRD pattern of the 1:6:20 condition if compared to the pattern for ZIF-8.

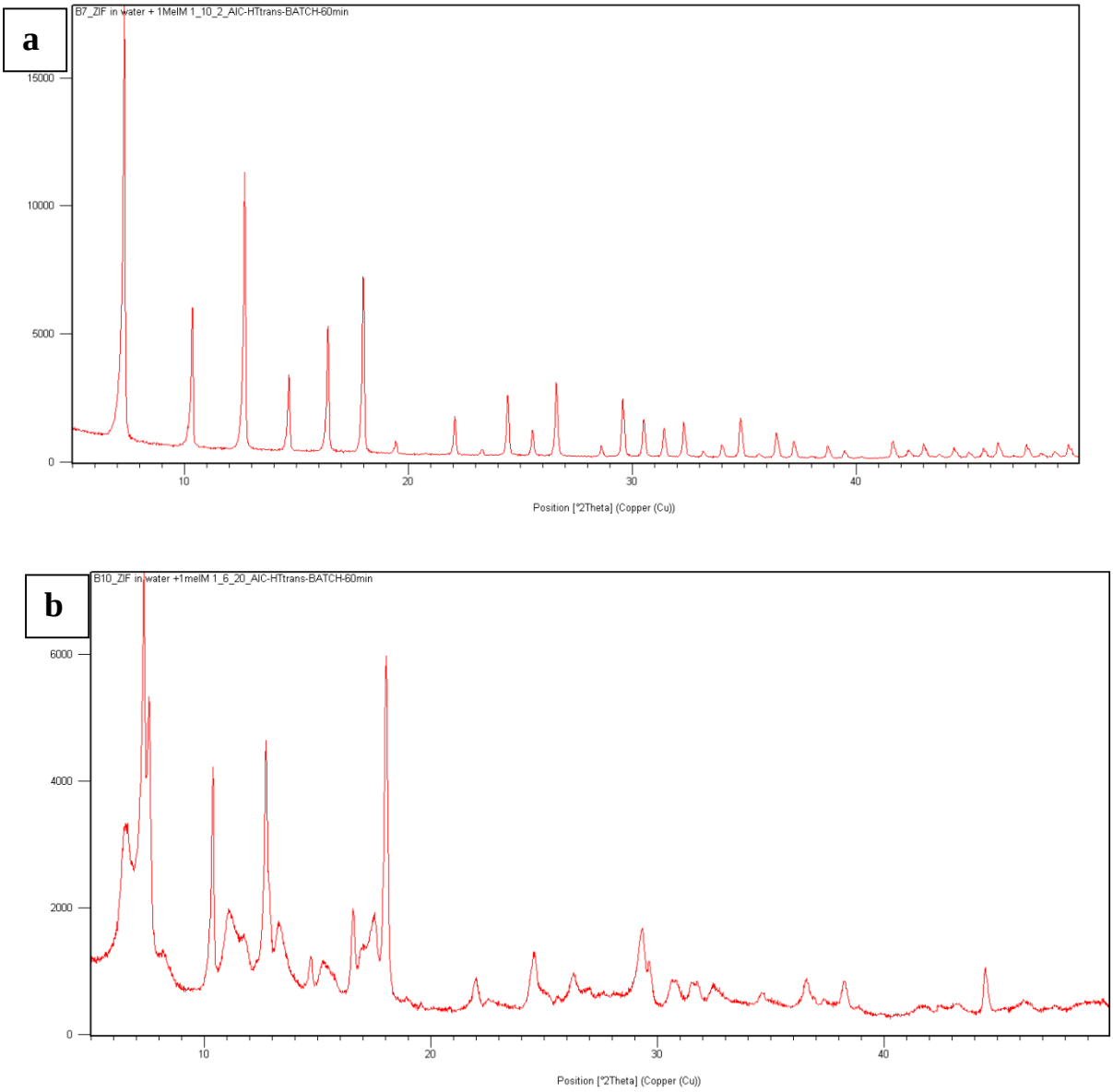


Figure 35- *XRD pattern for, (a)- ZIF-8, (b)- 1:6:20 condition RT.*

As is clearly seen, the ZIF-8 characteristic XRD peaks are all present in the 1:6:20 pattern, but there are more peaks than are usually seen. This means that there is probably a mixture of products with ZIF-8 formed and certainly a very crystalline complex has formed. The SEM image of the particles prepared in this condition can be seen in ***Figure 36***.

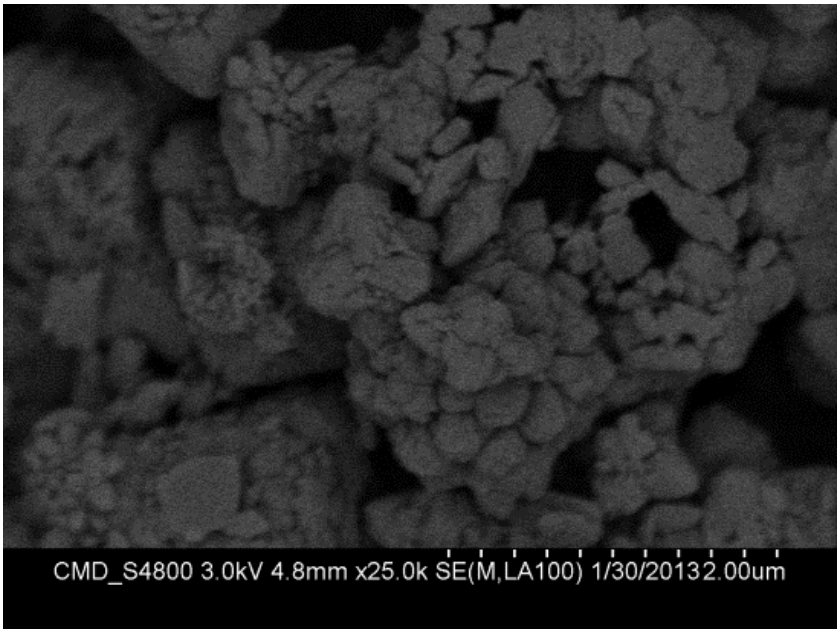


Figure 36*- SEM image of particles prepared in 1:6:20 condition, in water and RT.*

These particles are clearly much more crystalline than the "plate-like" particles produced in some of the other conditions, for example 1:1:0 as can be seen in ***Figure 31***.

So there seems to be some promise for these low 2-MeIM concentration conditions for preparing ZIF-8 however some additional encouragement may be needed. It was decided to try the low concentrations again but with a form of activation also being applied. This was done by carrying out the reactions at raised temperatures of 80°C in a heating block without stirring.

The conditions used were 1:3:X, 1:4:X, 1:6:X and 1:10:X, and 2 or 3 conditions were used for each of these sets of 2-MeIM concentrations. These are shown in the table, ***Table 4***.

***Table 4**- ZIF-8 + 1-MeIM in water at 80°C.*

Sample	Conditions	Observations
ZIF-8 + 1-MeIM	In water 11ml 1:3:3 (Zn:2-MeIM:1-MeIM) 80°C- heating block 24 hours	Very polydisperse, ZIF ranges from <500nm-5µm Very sharp peaks on XRD-highly crystalline
ZIF-8 + 1-MeIM	In water 11ml 1:6:0 80°C- heating block 24 hours	~500nm-3µm, Nano-aggregates to give microparticles? XRD shows ZIF-8 pattern- slightly broader peaks than 1:3:3
ZIF-8 + 1-MeIM	In water 11ml 1:6:6 80°C- heating block 24 hours	Particles range from <1µm-2µm, nice particle morphology Very sharp peaks on XRD-highly crystalline
ZIF-8 + 1-MeIM	In water 11ml 1:10:0 80°C- heating block 24 hours	Particles range from 500nm-1µm, nice particle morphology. Very sharp peaks on XRD-highly crystalline
ZIF-8 + 1-MeIM	In water 11ml 1:10:2 80°C- heating block 24 hours	Very nice particles, mostly cubes of about 400nm in size. Very sharp peaks on XRD-highly crystalline
ZIF-8 + 1-MeIM	In water 11ml 1:3:0 80°C- heating block 24 hours	**NOT ZIF-8-** plate like particles XRD shows the same pattern as for the 1:3:X at room temperature samples.
ZIF-8 + 1-MeIM	In water 11ml 1:3:1 80°C- heating block 24 hours	On the addition of a small amount of 1-MeIM ZIF-8 is able to form. Interesting particles- nano-aggregates, ~2.5µm in size Peaks in XRD slightly broader but is ZIF-8.
ZIF-8 + 1-MeIM	In water 11ml 1:4:0 80°C- heating block 24 hours	**NOT ZIF-8**-Shows more peaks than the signal for ZIF-8 however less noise in pattern than 1:3:0
ZIF-8 + 1-MeIM	In water 11ml 1:4:2 80°C- heating block 24 hours	XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 + 1-MeIM	In water 11ml 1:6:3 80°C- heating block 24 hours	XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 + 1-MeIM	In water 11ml 1:10:5 80°C- heating block 24 hours	XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.

The samples were submitted for SEM imaging as well as for XRD measurements and the difference to the room temperature syntheses was quite significant. The yields of these reactions in comparison to those prepared at room temperature are dramatically higher with yields of >60% for most of the reactions. This is in comparison to the very low yields for the room temperature reactions which were sometimes incredibly low. The yields for these elevated temperature reactions reduce as the amount of 1-MeIM increases but more significantly as the 2-MeIM concentration increases. This can be linked to the competition

between the 1-MeIM acting as a modulator through deprotonation or through coordination as the concentrations of reactants changes. This is because when the 2-MeIM concentration increases, 1-MeIM acts as a modulator through reducing the nucleation rate, reducing the amount of particles formed. But when the 2-MeIM is low the 1-MeIM acts as a modulator through increasing the rate of nucleation and making more particles and increasing the yield.

The only samples which had not successfully formed ZIF-8 were the 1:3:0 and the 1:4:0 conditions, without any 1-MeIM present. This shows that the addition of a small amount of 1-MeIM and the added activation from the elevated temperature allows the ZIF-8 to form even at these low 2-MeIM concentrations.

As well as this, the 1:4:0 condition seems to have almost made the ZIF-8 successfully, with the XRD pattern looking similar to that of the known ZIF-8 pattern. There are extra peaks but the ZIF-8 peaks are also apparent. This can be seen in the XRD pattern below, ***Figure 37***.

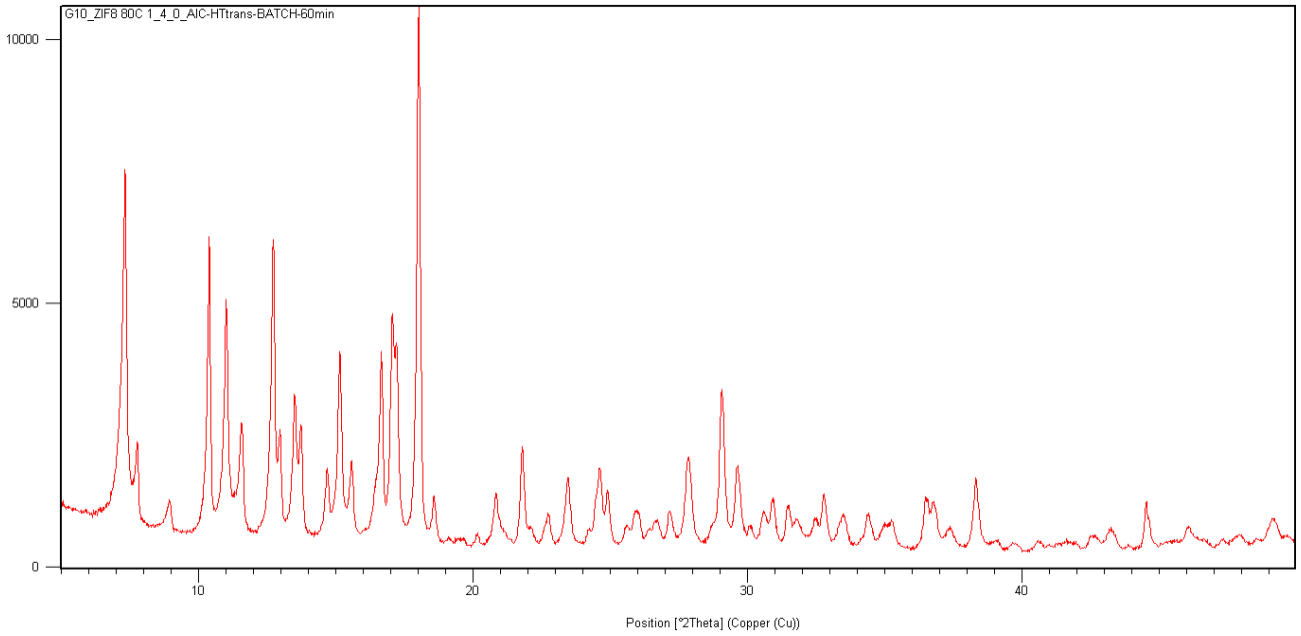
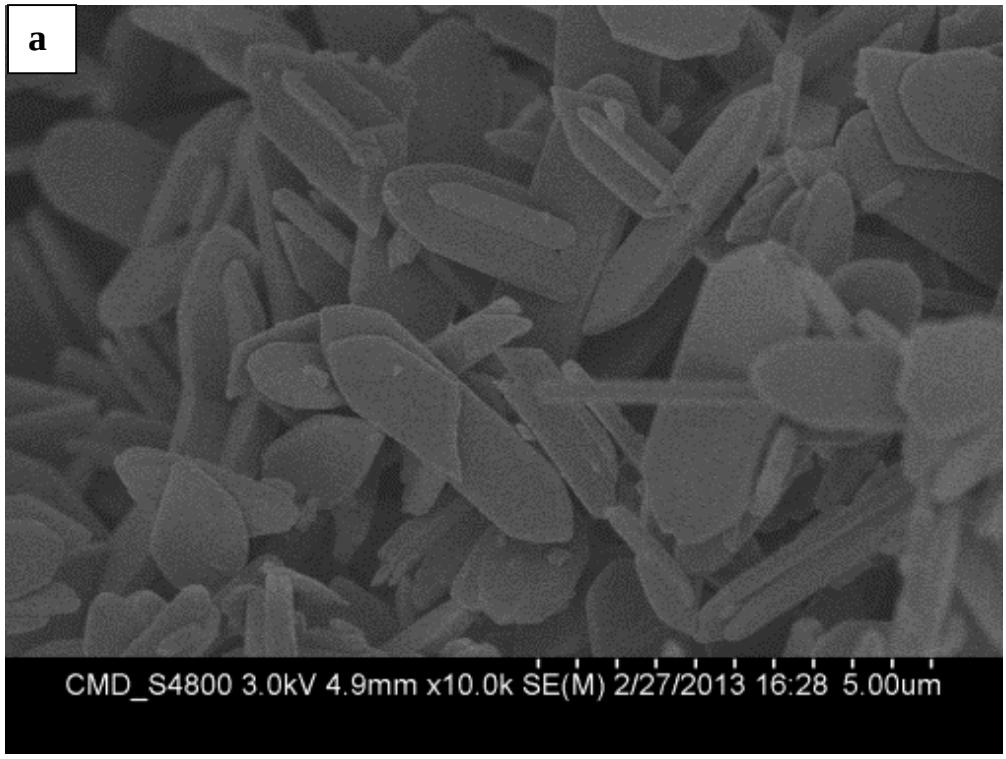


Figure 37- *XRD pattern of "ZIF-8" +1-MeIM 1:4:0 in water 80°C*

These particles can clearly be seen to be crystalline and therefore the presence of 1-MeIM combined with the heating is producing the desired effect, to encourage the formation of the crystalline product.

Some of these particles produced had strange morphologies. Starting with the 1:3:X conditions the 1:3:0 condition again produced the "plate-like" particles seen for the room temperature synthesis which can be seen in ***Figure 38***. These particles are crystalline, seen in the XRD pattern (***Figure 39***), but they are not ZIF-8 as there are too many peaks in the pattern. However, the patterns for ZIF-8 could be in amongst these peaks as there are signals showing at the right places for ZIF-8.



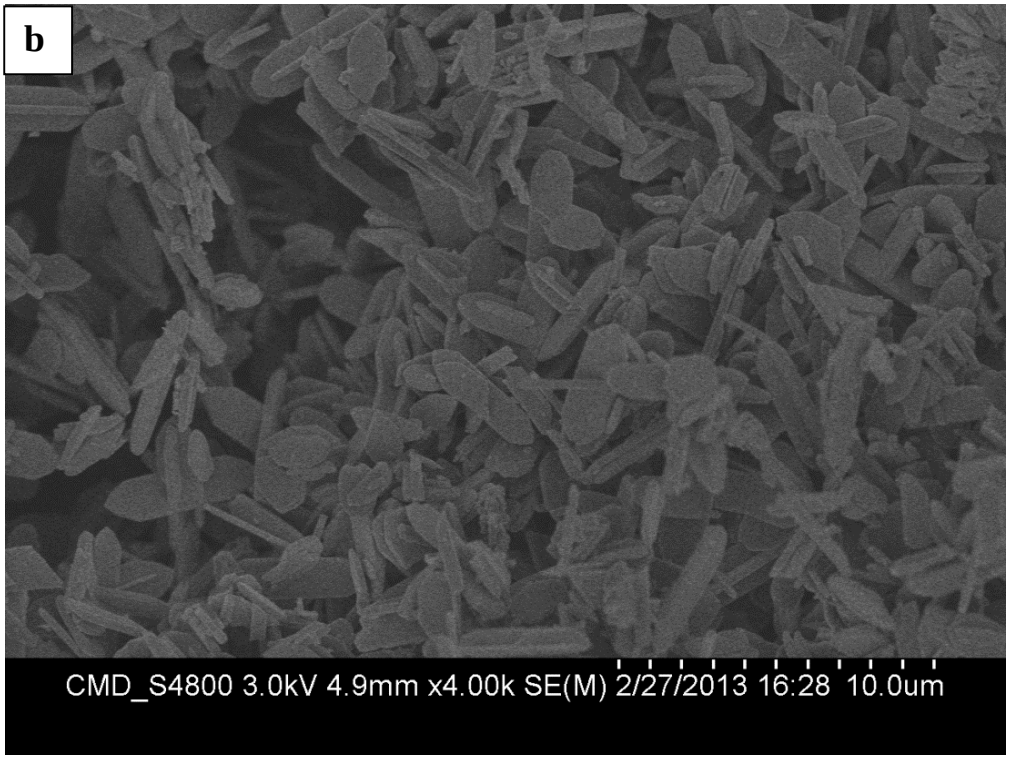


***Figure 38**- "Plate-like" particles produced in 1:3:0 in water at 80°C.*

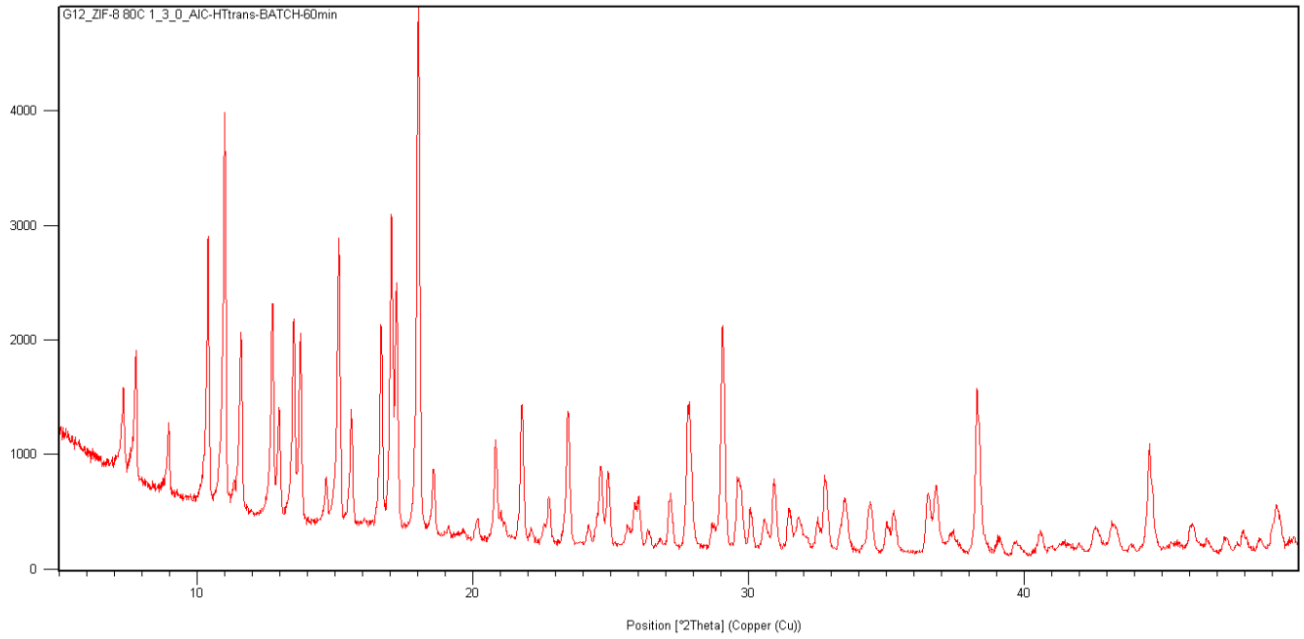


***Figure 39**- XRD pattern for "plate-like" particles 1:3:0 80°C*

It was again decided to test the 1:3:0 particles for their BET surface area values to see whether the elevated temperatures had started to make these particles porous. The SEM images in ***Figure 38*** show the strange "plate-like" particles that formed. These particles are more crystalline looking than the ones produced at room temperature so it was thought that they may have formed more porous structures.

The nitrogen adsorption isotherm of these particles is shown in ***Figure 40***.

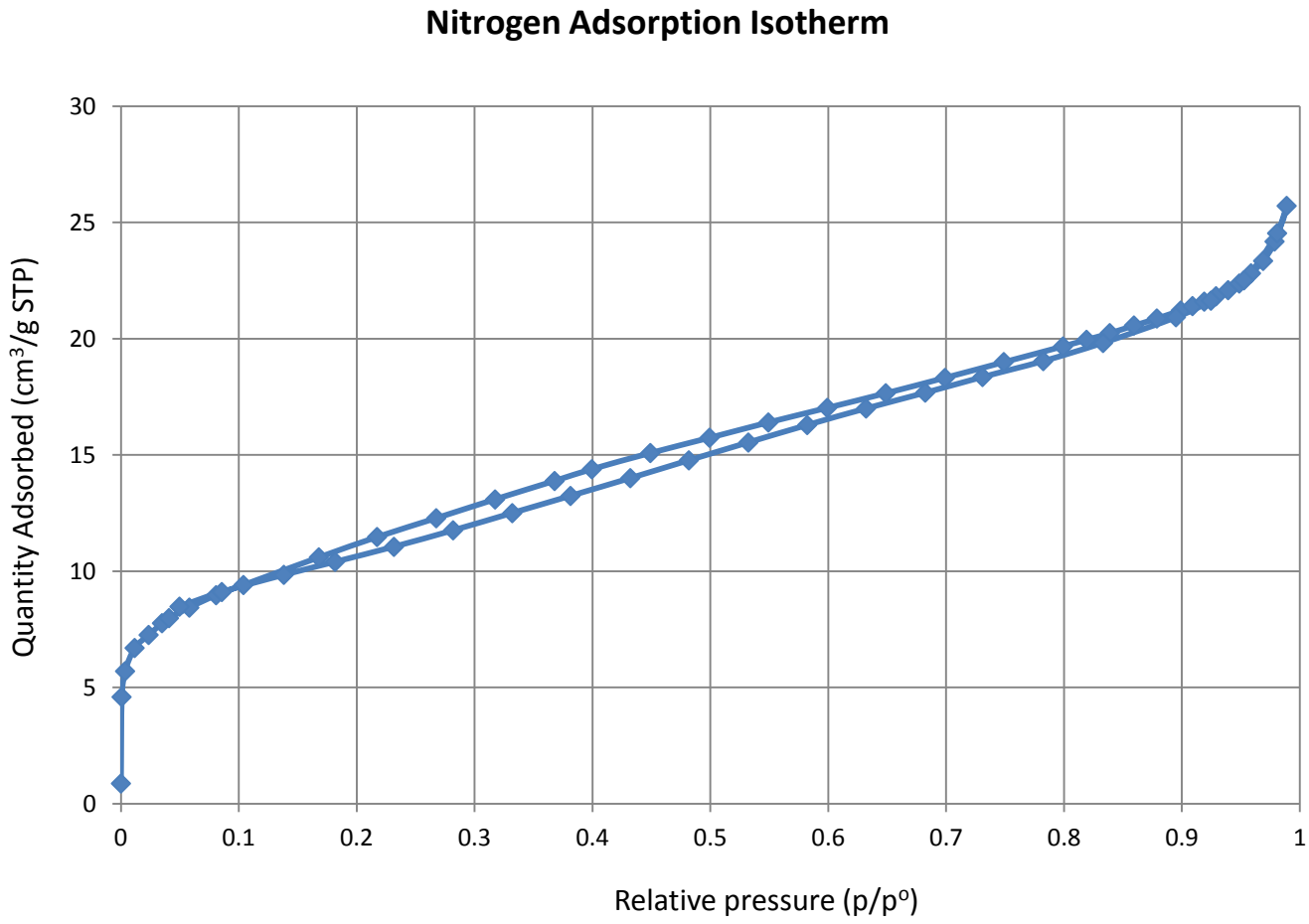


Figure 40- *N_2 adsorption isotherm for "plate-like" particles 1:3:0 80°C*

These particles had a larger BET surface area than of those prepared in the room temperature condition, with a BET surface area of 36 m^2g^{-1}. This shows that these particles must be slightly more porous than those prepared in the room temperature condition and the hysteresis loop in the isotherm shows that there are some mesopores present in the particles. This is consistent with the BJH average pore width value of 4.2 nm. They are not however porous enough for us to use in place of ZIF-8 which has BET surface area of ~1600 m^2g^{-1}.

Unlike in the room temperature synthesis, when the reaction is carried out at elevated temperatures and just a small amount of 1-MeIM is added, the formation of ZIF-8 is successful, with the 1:3:1 condition producing ZIF-8 which can be seen from the XRD pattern in ***Figure***

41. Although there are a few very small peaks which aren't usually seen for ZIF-8 which could mean that there is a small amount of another compound present.

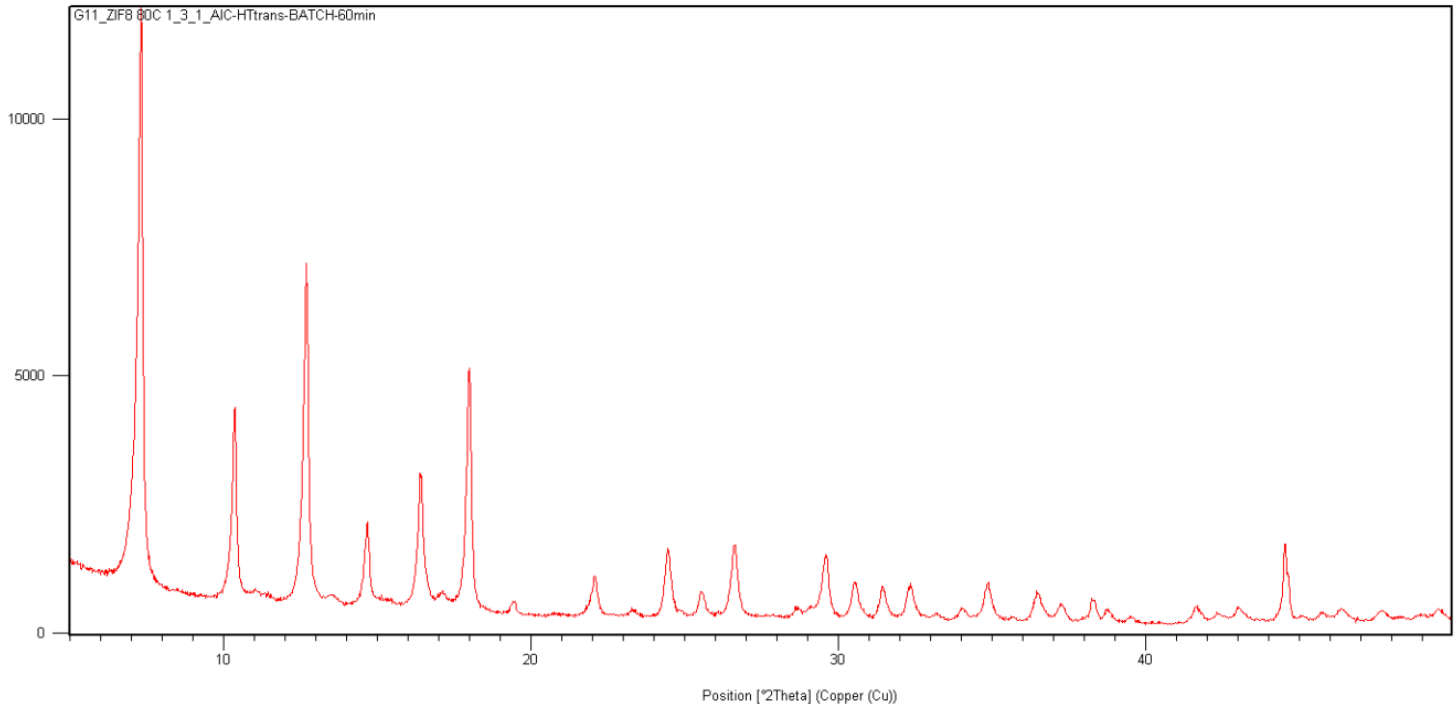


Figure 41– *XRD pattern of ZIF-8 + 1-MeIM at 80°C 1:3:1 nano-aggregates*

The particles produced in this condition are very interesting looking indeed. They seem to be nanoparticles which have aggregated together to produce microparticles. This could be possibly very interesting, as it could increase the surface area of the particles dramatically. It could also cause the particles to be hierarchically porous, with micro- meso- and macropores present in the frameworks of the ZIF-8 crystals. These nano-aggregates can be seen in ***Figure 42*** and the interesting morphology can be easily seen. The particles are also very monodisperse with a diameter of ~2.5 µm. These particles were thought to be a good choice for taking on further into the next stages of our study, the preparation of ZIF-8/polymer composite materials.

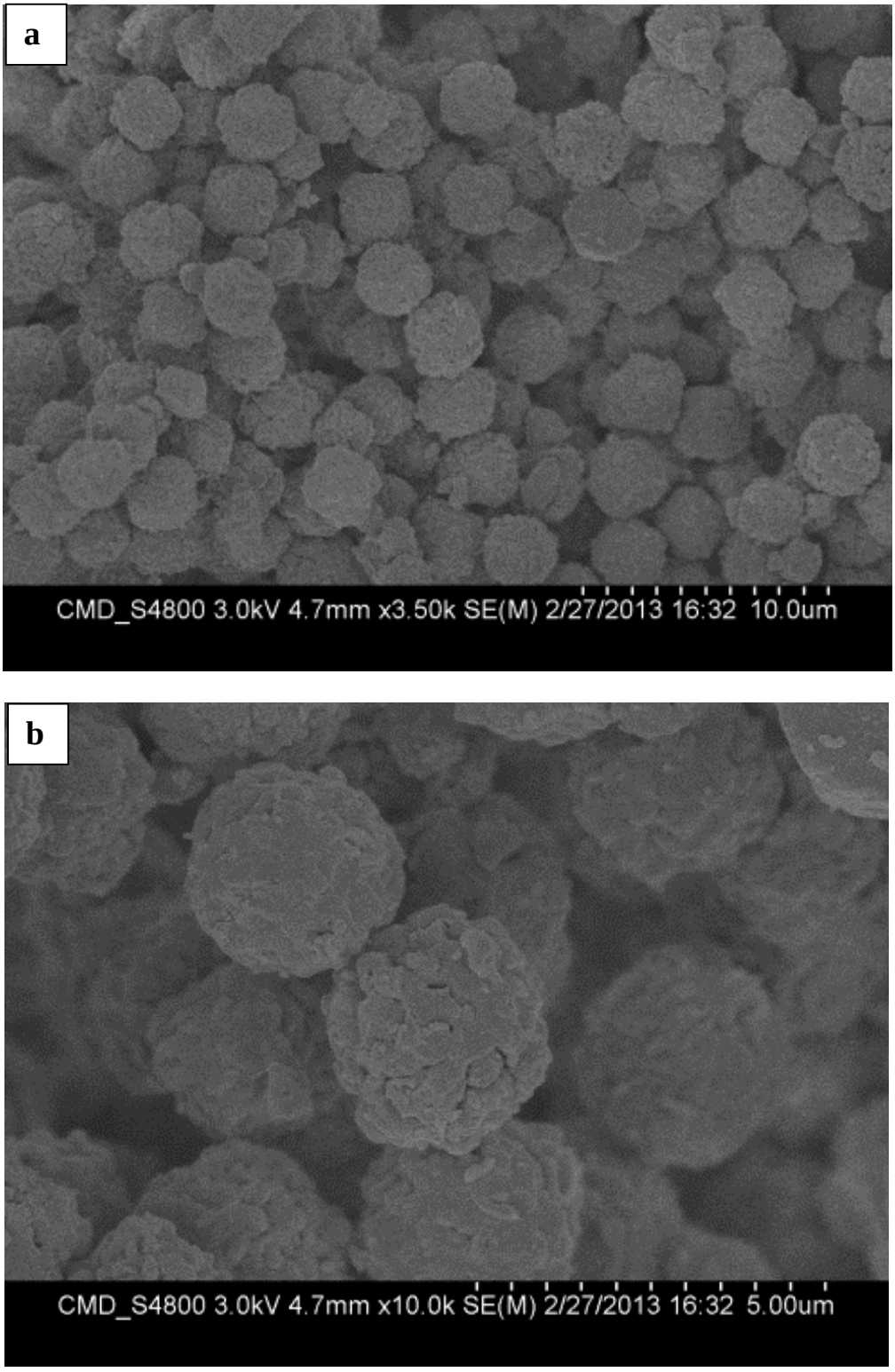


Figure 42*- ZIF-8 + 1-MeIM 1:3:1 80°C "nano-aggregates".*

Similarly to the 1:3:X case, the 1:4:X conditions also were unsuccessful with no 1-MeIM, but on the addition of a small amount of 1-MeIM the ZIF-8 formed and gave particles of ~2 μm with relatively good monodispersity (***Figure 43***). The nano-aggregate particles are not formed

however and the particles haven't got very uniform or well defined shapes, so these particles were not chosen to take forward any further.

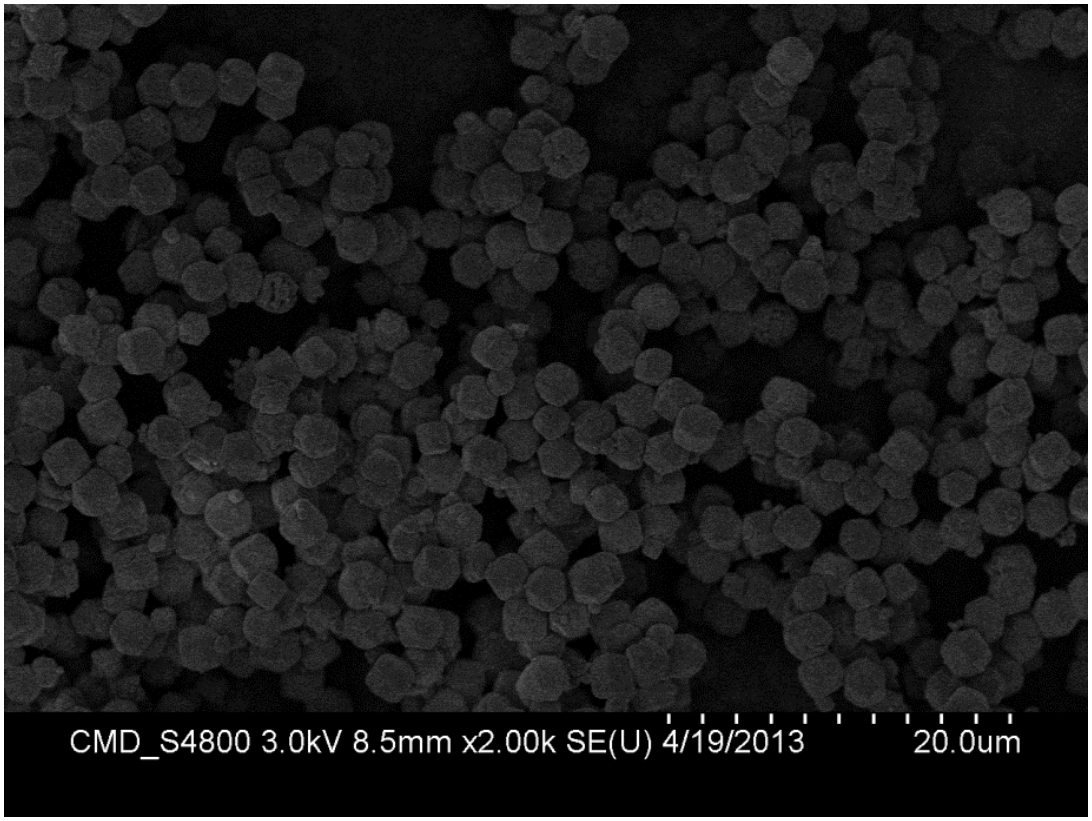


***Figure 43**- ZIF-8 +1-MeIM 1:4:2 80°C.*

When the 2-MeIM concentration was increased to 1:6:X the ZIF-8 formed even in the absence of 1-MeIM. This means that the heat activation is stimulating the reaction to happen successfully when this wasn't possible at room temperature. The particles formed have unusual morphologies and again seem to be these nano-aggregate particles, ***Figure 44***. The XRD pattern shows very sharp peaks which show that, although the particles don't look particularly crystalline, they are highly crystalline species, ***Figure 45***.

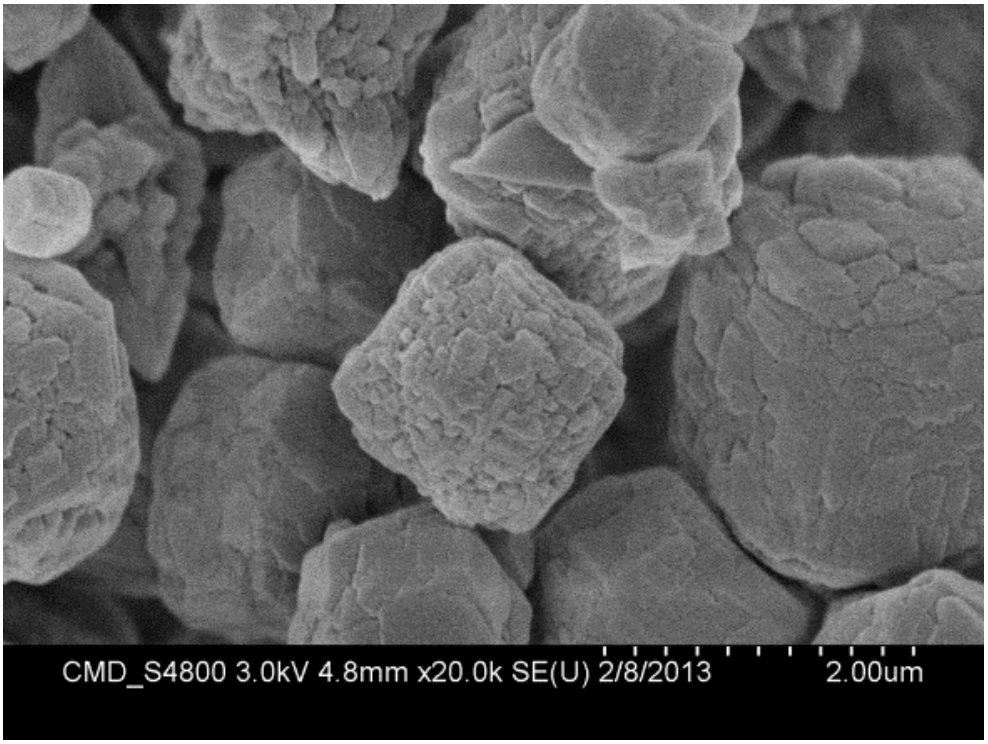


***Figure 44**- ZIF-8 +1-MeIM 1:6:0 80°C "nano-aggregates".*

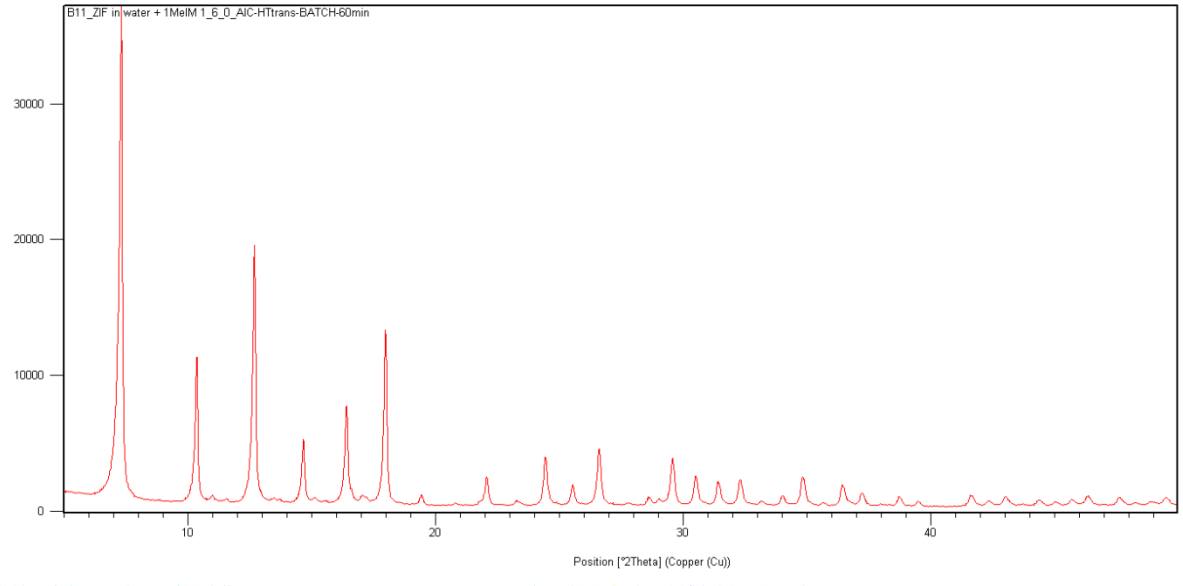


***Figure 45**- XRD pattern of ZIF-8 1:6:0 80°C "nano-aggregates".*

These particles, with their unusual nano-aggregate type morphologies, were thought to be interesting and the surface area measurements were decided to be taken. The nitrogen adsorption isotherm for these particles can be seen in ***Figure 46***.

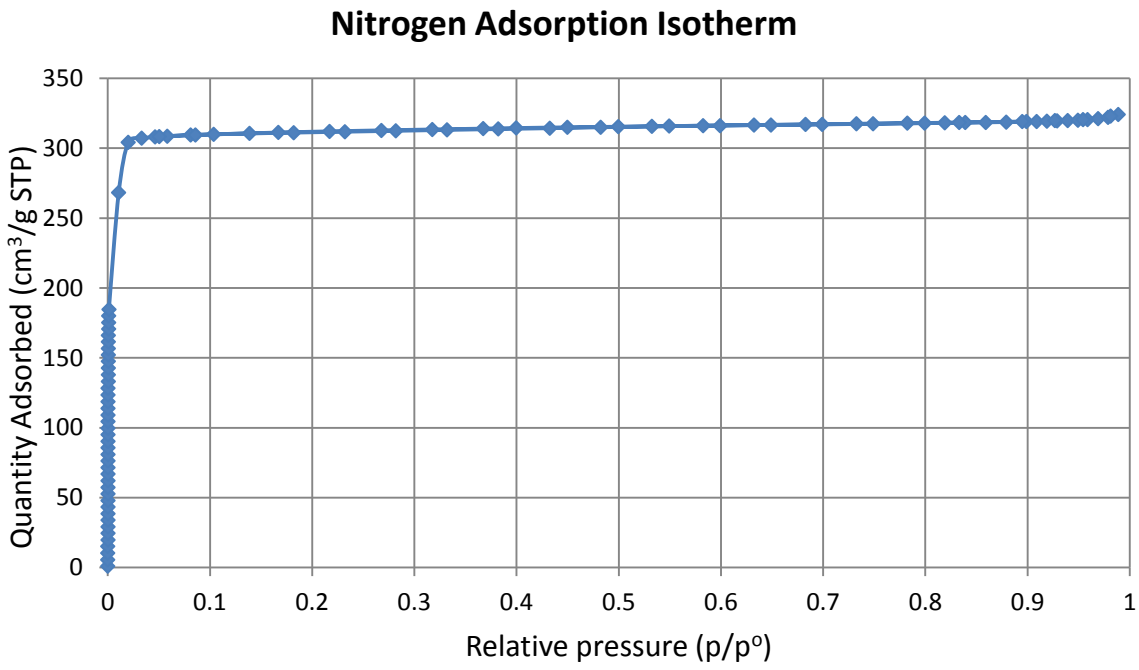


***Figure 46**- N_2 adsorption isotherm for ZIF-8 particles "nano-aggregates" 1:6:0 80°C*

This Type I isotherm indicates that these particles are predominantly microporous rather than mesoporous. The BET surface area of these particles was 1315 m^2g^{-1} which is significantly higher than the "plate-like" particles previously measures. These ZIF-8 particles have not, however, got as high a BET surface area as has previously been recorded for ZIF-8 particles which makes them less attractive for further development.

When the ratio was increased to 1:6:3 and also 1:6:6, the particles formed increased in crystallinity with the particles having very attractive morphologies and particle sizes between 750 nm and 1µm. This again shows that the trend seen in MeOH is not the same in water reactions, as the addition of more 1-MeIM in the Methanol solvent caused an increase in particle size which isn't seen here. In the water reactions the addition of 1-MeIM seems to cause improved particle formation and crystallinity of the product rather than changing the particle size much. It seems to be the changing of the 2-MeIM concentration which affects the size of the particles formed when carrying out the reactions in water.

This is also seen in the 1:10:X reactions, with the particles formed in the 1:10:2 condition showing much improved particle morphology and monodispersity in comparison to the 1:10:0 condition.

The 1:10:2 particles are much smaller than the others prepared in these high temperature reactions with particle sizes of ~400 nm and nice cube shaped particles and very sharp peaks in the XRD pattern. These particles, shown in ***Figure 47***, were chosen to take forward into the further stages of our study due to their uniform size and shape and the 400 nm particle size which is an ideal size for our requirements. The sharp peaks in the XRD pattern (***Figure 48***) show that the particles are very crystalline and this supports our idea that the presence of 1-MeIM is aiding the particle formation and improving the crystallinity of the ZIF-8 framework structures.

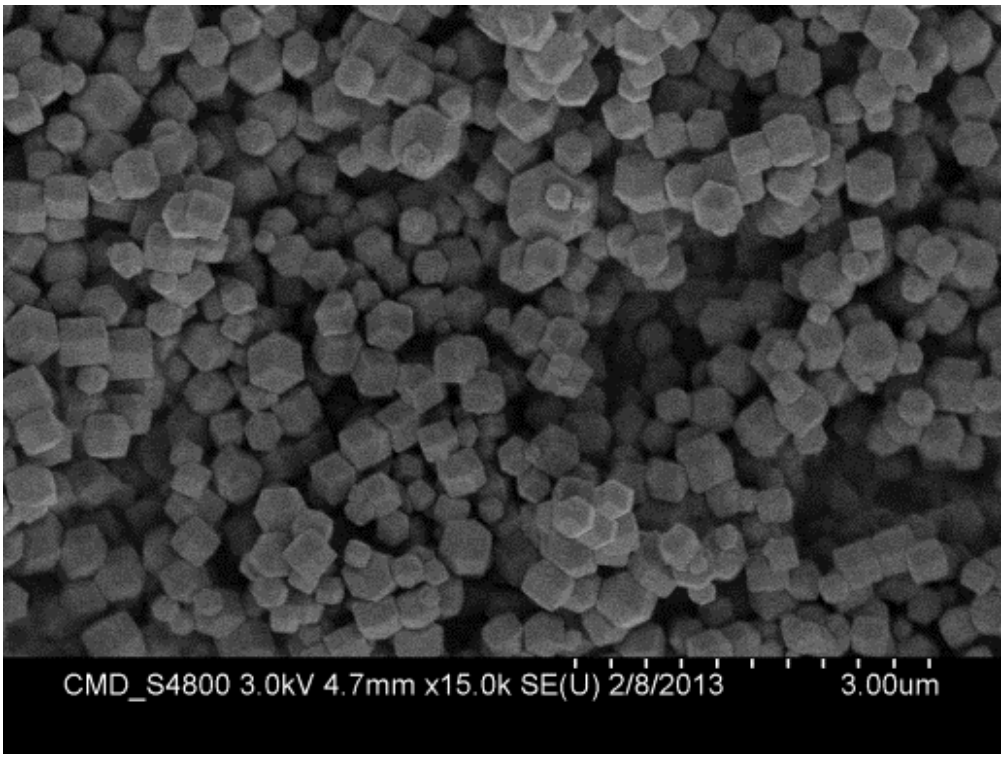


Figure 47*- ZIF-8 +1-MeIM 1:10:2 80°C.*

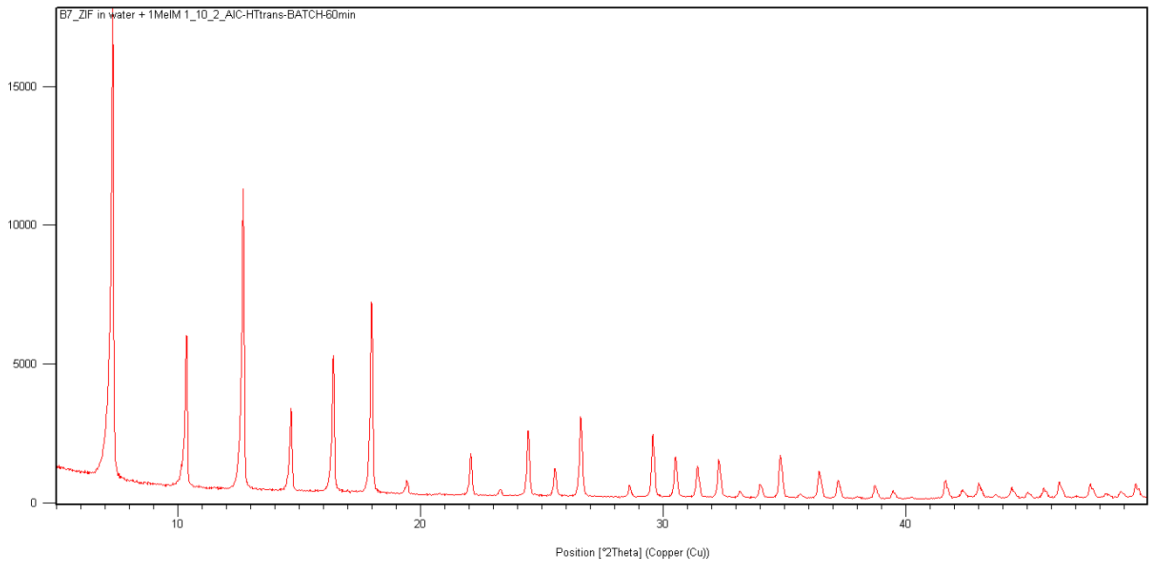


***Figure 48**- XRD pattern 1:10:2 80°C.*

When the ratio was increased to 1:10:5 the particle sizes dropped to 300nm and therefore this shows again that the trend seen in methanol with the addition of 1-MeIM is not seen in water, and in this case, is actually having the opposite effect, reducing the particle size as the concentration of 1-MeIM is increased. The particle size dropped 1:10:0 to 1:10:2 to 1:10:5 from 1 µm to 400 nm to 300 nm. This is a significant change in size and therefore at this concentration of 2-MeIM, altering the 1-MeIM concentration can be used to precisely control the particle size of the ZIF-8 crystals.

To test whether the increase in temperature can again be used to improve the formation of ZIF-8 particles, we decided to test some of these conditions at an even higher temperature; under solvothermal conditions at 120°C in stainless steel Teflon lined autoclaves.

The concentrations chosen were 1:3:X, 1:4:X and 1:6:X and the exact conditions can be seen in the table below (***Table 5***).

***Table 5**- ZIF-8 +1-MeIM solvothermal conditions 120°C.*

Sample	Conditions	Observations
ZIF-8 + 1-MeIM	In water 6ml 1:3:0 (Zn:2-MeIM:1-MeIM) 120°C- autoclave 24 hours	**Not ZIF-8-** plate like particles XRD shows same pattern as 1:3:0 at 80°C and also the 1:3:x samples at RT
ZIF-8 + 1-MeIM	In water 6ml 1:3:3 120°C- autoclave 24 hours	Polydisperse, 500nm-5µm XRD shows the characteristic pattern of ZIF-8 with nice sharp peaks.
ZIF-8 + 1-MeIM	In water 6ml 1:6:0 120°C- autoclave 24 hours	Nano-aggregates? ~2µm XRD shows characteristic pattern of ZIF-8 but has slightly broad peaks
ZIF-8 + 1-MeIM	In water 6ml 1:6:6 120°C- autoclave 24 hours	Polydisperse, sizes ranging 250nm-2.5µm, nice particle morphology XRD shows characteristic pattern of ZIF-8 and has sharp peaks
ZIF-8 + 1-MeIM	In water 6ml 1:3:1 120°C- autoclave 24 hours	Polydisperse particles ~1-5 µm, ZIf-8 shown by characteristic pattern in XRD
ZIF-8 + 1-MeIM	In water 6ml 1:6:3 120°C- autoclave 24 hours	Nicely formed particle of ~1 µm, pure-phase ZIF-8 from XRD pattern

The yields in these reactions were very similar to those of the reactions in the 80°C conditions with the yield reducing with an increase in both 1-MeIM and 2-MeIM but the 2-MeIM having the most profound effect. This is because when the 2-MeIM concentration increases, 1-MeIM acts as a modulator through reducing the nucleation rate, reducing the amount of particles formed. But when the 2-MeIM is low the 1-MeIM acts as a modulator through increasing the rate of nucleation and making more particles and increasing the yield. The solvothermal reaction of the 1:3:0 condition, similarly to the room temperature and 80°C reactions, did not successfully form ZIF-8 crystals, instead producing the "plate-like" particles seen in previous reactions. These particles are crystalline but do not have the characteristic XRD pattern of ZIF-8 crystals. The particles can be seen in ***Figure 49*** and they show the same or similar morphology to the other low concentration products produced in the different temperature conditions.

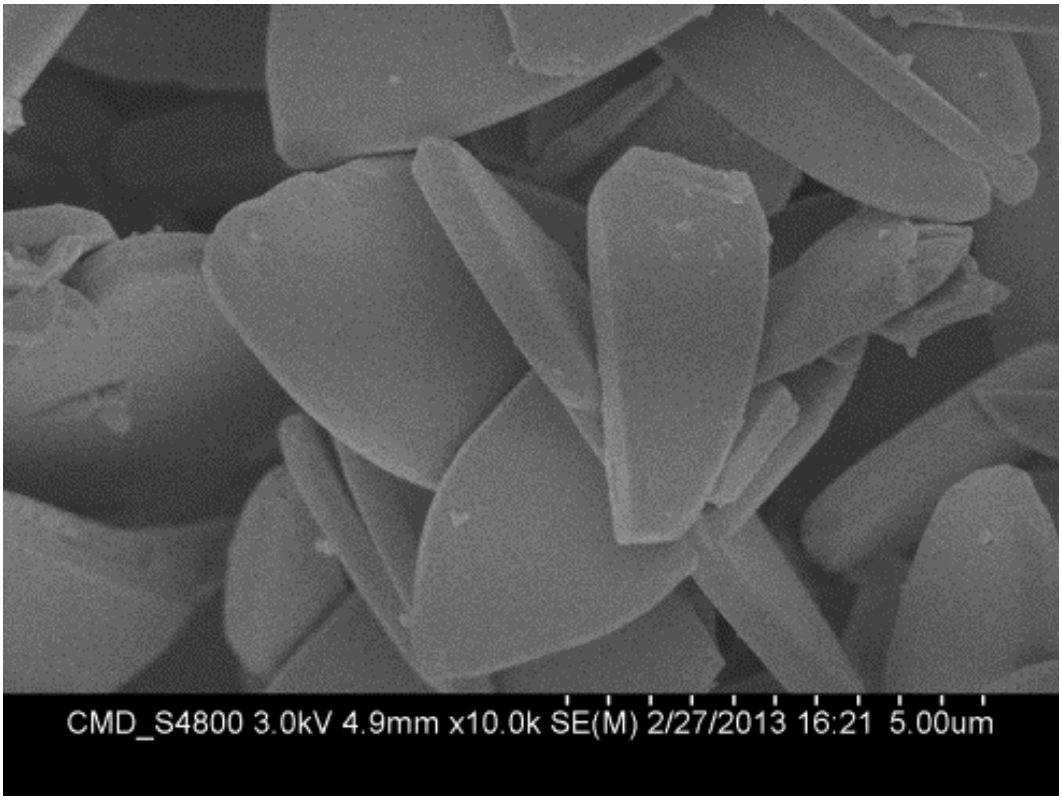


***Figure 49**- "Plate-like" particles produced in 1:3:0 solvothermal reaction.*

This concentration of 2-MeIM is just too low for the successful formation of ZIF-8 without the presence of the auxiliary ligand to aid in the crystallisation process. This is shown by the next reaction attempted, the 1:3:1 condition, where the ZIF-8 framework did form successfully and the particles have got a certain level of definition to their shape. The ZIF-8 produced in this condition was however very polydisperse (***Figure 50***) and didn't have the same interesting "nano-aggregate" structure as the particles formed in the same conditions but at 80°C. This may be due to the improved crystallinity due to the presence of the 1-MeIM being further enhanced by the more intense activation of the higher temperatures and pressures in this solvothermal method. That aside it is a significant change in particle morphology and crystallinity of the product with such a small change in the reaction conditions. This gives great scope for manipulation of the particle sizes and shapes with a view to produce certain morphologies based on the needs for specific applications.[9, 10, 15, 17, 36, 56, 69]

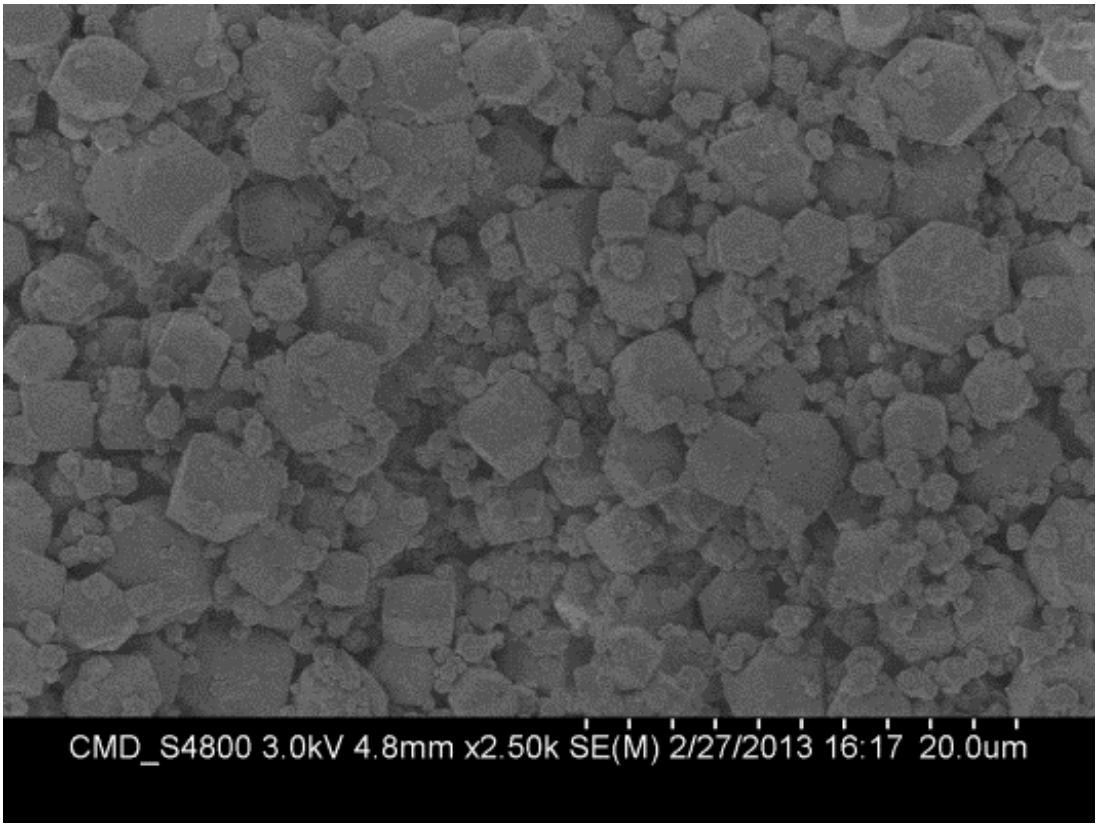


***Figure 50**- ZIF-8 + 1-MeIM 1:3:1 120C solvothermal conditions.*

The 1:6:X series are very alike the corresponding reactions in the 80°C reactions, with the 1:6:0 condition producing the "nano-aggregate" particles again with the very interesting morphologies. They are however much more monodisperse than their 80° counterparts which shows that the crystallization process has again been improved by the combination of the added 1-MeIM ligand as well as the extra activation from the solvothermal conditions. The line-broadening in the XRD pattern also supports the idea that these are nanoparticles which have aggregated together, as this phenomenon occurs with nanomaterials in XRD patterns. This can be seen in ***Figure 51***, the XRD pattern for these nano-aggregates, which shows the broad peaks but still gives the characteristic ZIF-8 pattern.

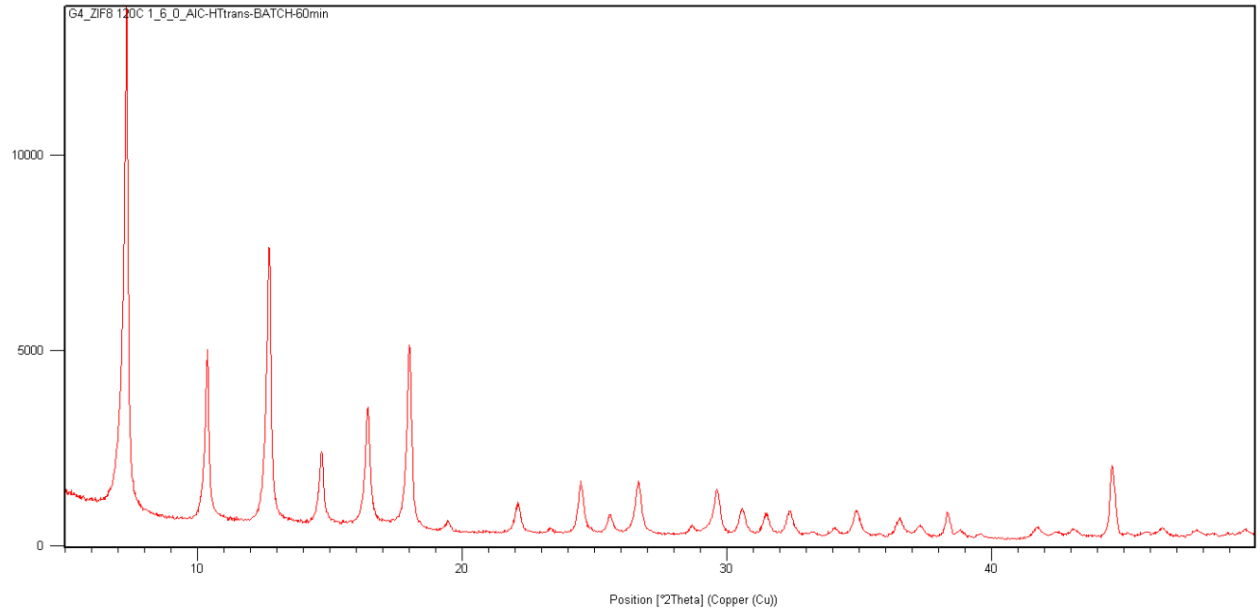


Figure 51*- ZIF-8 "nano-aggregates" 1:6:0 with line broadening caused by nanoparticles.*

The increase in particle size with added 1-MeIM that was seen in methanol is again absent in this series of reactions, with the size dropping from ~1.5 µm to ~ 1µm from the 1:6:0 condition through to the 1:6:6 condition. This however is not a great difference if you consider that there were 4 different conditions in between all with overlapping particle size ranges. So again the fact that the 1-MeIM is acting as an aid in the crystallization process is apparent, and it is clear that the trend seen for methanol is not occurring when water is used as the solvent.

This is a positive thing as it will allow for much more precise control of the particle shape and size, controlling size be varying the 2-MeIM concentration and controlling shape and crystallinity with the 1-MeIM concentration.

There have been studies previously which have found that varying the temperature of these types of reactions can change the role that the auxiliary ligand plays in the modulation of the reaction. Cravillon et al[70] investigated the formation of ZIF-8 under solvothermal conditions and in the presence of sodium formate as the modulating ligand. They compared their findings to those of a previous study which had done the same reactions but at room temperature. They found that at room temperature the sodium formate modulates the formation of the ZIF-8 particles by coordination competition as we think our reactions are being controlled by.[35] But they discovered that at raised temperatures, under solvothermal conditions, the reaction

switches to being controlled by deprotonation equilibria as is usually seen for stronger basic ligands than these.[70] This could be because, at room temperature the higher concentration of 2-MeIM needed gives a high nucleation rate and therefore the auxiliary ligand acts to slow the nucleation rate down and therefore in room temperature synthesis the reaction produces less particles which grow to larger sizes, and this effect increases with the concentration of auxiliary ligand. This is the effect we saw when carrying out our ZIF-8 synthesis in methanol, but it is not what was seen in the case of water even in the room temperature case. This shows that there must also be some effect from the solvent which is changing the role of the modulating ligand. At increased temperatures, or in water as we've seen, the concentration of 2-MeIM used can be much lower and therefore the auxiliary ligand acts as an accelerator to the nucleation process and there are therefore more particles which can't grow as large.

A possible reason for the different effects in methanol than in water is the role of the solvent in the reaction. The polarity of the solvent as well as the solubility of the reactants in the solvent can have large effects on the particles formed and this has been studied by several research groups who have showed that the choice of solvent can dramatically change the framework structures of the particles formed.[8, 71, 72] This has been seen in the paper by Long et al[71] (2011) who synthesised two different MIL species depending on the solvent used. They did their reactions in DMF, ethanol, water, acetone and ethanol/water, methanol/water or acetone/water mixtures, and found that altering the solvent has a profound effect on the product produced. In their study, starting from the same reactant mixtures but using different solvents, they obtained completely different MOF structures, so the effect of the solvent chosen is clearly dramatic.

Another possible effect could be the pH of the solutions depending on the amounts of 2-MeIM and 1-MeIM present, as this has also been found to effect the formation of particles and the morphologies and framework structures of those particles.[72]

It has also been suggested that the volume of solvent used and hence the dilution of the reaction may have an effect on the particle formation. The reactions we carried out in methanol were in much larger volumes of solvent and therefore were much more dilute reactions. The reactions we carried out in water were in much smaller volumes, generally less than 20 ml in comparison to 100 ml for the methanol synthesis. This means that the reaction mixture is much more concentrated. This effect has been witnessed in other research and has been attributed to a competition between the formation of the kinetically favoured phase and the thermodynamically favoured phase.[72]

Conclusion

The preparation of ZIF-8 in water has been successful under many different conditions with different temperatures and different concentrations being used as well as preparation in the presence of auxiliary ligands. The use of auxiliary ligands has been successful in allowing the size-control of the ZIF-8 particles synthesised and this can be exploited in order to produce ZIF-8 of specific, chosen sizes for use in applications which have a size-specificity. For the preparation of ZIF-8@polymer composite materials the size range of ZIF-8 chosen to be suitable was between 100nm and 2µm and the particles would have to be relatively monodisperse and have well-defined crystalline structures. The particles which best meet these requirements are the ZIF-8 prepared in the presence of auxiliary ligands, sodium formate and 1-methyl imidazole. The size of these particles can be controlled by altering the concentration of these two auxiliary ligands. Another thing that changes with concentration of these ligands is the monodispersity of the sample and also the particle morphology. This could also be exploited if particles of a particular morphology were required or desired.

The three ZIF-8 samples that were chosen to be taken forwards into the next stage of the invstigation, the preparation of ZIF-8@polymer composites, were the Zn:2-MeIM:1-MeIM in water under the conditions: 1:20:20 at room temperature, 1:10:2 at 80°C and 1:3:1 at 80°C. These 3 ZIF-8 samples were used to continue our work further, by developing novel methods of composite preparation.

3.3 Experimental

All materials used were purchased from Sigma Aldrich and required no further purification.

3.3.1 ZIF-8 synthesis- A method used previously in the group

$Zn(NO_3)_2.6H_2O$ (146.8mg, 0.0493mmol) was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM (2.8341g, 0.0345mol) in 10ml H_2O with stirring. This was left stirring for 24 hours. It was then centrifuged, washing 3 times with water. It was then dried in the vacuum oven overnight and then submitted for SEM imaging and XRD.

3.3.2 ZIF-8 in water RT 1:20 (Mass ratio Zn:2-MeIM)

$Zn(NO_3)_2.6H_2O$ (148.1mg, 0.0493mmol) was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM (2.8348g, 0.0345mol) in 10ml H_2O with stirring. This was left stirring for 24 hours. It was then centrifuged, washing 3 times with water.

3.3.3 ZIF-8 in water 1:40 (Mass ratio Zn:2-MeIM)

$Zn(NO_3)_2.6H_2O$ (146.5mg, 0.0493mmol) was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM (5.8686g, 0.0715mol) in 10ml H_2O with stirring. The 2-MeIM had to be heated to dissolve. This was left stirring for 24 hours. It was then centrifuged, washing 3 times with water. This was submitted for SEM imaging.

3.3.4 ZIF-8 preparation in water + 1-MeIM

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (g)	Mass 1MeIM (g)
1:10:0	149.5	1.4858	0
1:10:5	149.1	1.4887	0.7485
1:10:10	149.0	1.4883	1.4788
1:20:0	147.7	2.9425	0
1:20:10	149.4	2.9872	1.4805
1:20:20	146.6	2.9813	2.9448
1:30:0	148.8	4.4335	0
1:30:15	148.8	4.4430	2.2254
1:30:30	149.1	4.4315	4.4731
1:40:0	147.9	5.9279	0
1:40:10	148.8	5.9580	1.4722
1:40:20	147.4	5.8967	2.9602

The $Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this the solution of 2-MeIM and 1-MeIM in 20ml H_2O was added with stirring. This was left stirring for 24 hours. They were then centrifuged and washed three times with water. They were submitted for SEM imaging.

3.3.5 ZIF-8 preparation in water + sodium formate

1:30:30- $Zn(NO_3)_2.6H_2O$ (148.9mg, 0.0501mmol) was dissolved in 1 ml H_2O and to this was added a solution of 2MeIM (4.4391g, 0.0150mol) and sodium formate (4.4237g, 0.0150mol) in 19ml H_2O with stirring. This was left stirring for 24hours and then it was centrifuged and washed 3 times with water. It was then submitted for SEM imaging.

1:20:20- $Zn(NO_3)_2.6H_2O$ (148.9mg, 0.0501mmol) was dissolved in 1 ml H_2O and to this was added a solution of 2MeIM (2.9961g, 0.0100mol) and sodium formate (2.9769g, 0.0100mol) in 19ml H_2O with stirring. This was left stirring for 24hours and then it was centrifuged and washed 3 times with water. It was then submitted for SEM imaging.

3.3.6 ZIF-8 preparation in water + 1-MeIM

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1MeIM (g)
1:1:0	147.0	148.6	0
1:1:1	149.3	146.8	0.1482
1:1:10	146.5	149.8	1.4867
1:1:20	150.9	147.1	2.9555
1:3:0	148.1	446.7	0
1:3:3	149.7	445.8	0.4597
1:3:10	150.3	447.8	1.4779
1:3:20	149.5	444.5	2.9299
1:6:0	149.7	888.8	0
1:6:6	150.4	892.2	892.9
1:6:10	149.3	887.5	1.4903
1:6:20	145.9	888.1	2.9469

The $Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this the solution of 2-MeIM and 1-MeIM in 20ml H_2O was added with stirring. This was left stirring for 24 hours. They were then centrifuged and washed three times with water. They were submitted for SEM imaging.

3.3.7 ZIF-8 preparation in water + 1-MeIM at 80°C

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)	Yield (%)
1:3:3	146.3	443.2	446.0	37.7
1:6:0	150.0	883.9	0	91.2
1:6:6	145.6	885.8	888.1	43.5
1:10:0	146.6	1493.9	0	72.7
1:10:2	145.3	1483.8	301.8	65.0

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 10ml H_2O. These were placed in the heating block at 80°C for 24 hours. These were centrifuged and washed 3 times with H_2O. They were then submitted for SEM and XRD.

3.3.8 ZIF-8 preparation in water + 1-MeIM at 120°C

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)	Yield (%)
1:3:0	75.0	221.3	0	91
1:3:3	76.6	228.0	247.9	45
1:6:0	76.3	444.4	0	81
1:6:6	75.9	445.8	448.0	47

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 5ml H_2O. These were placed in Teflon lined stainless steel autoclaves and then placed in a conventional oven at 120°C for 24 hours. These were centrifuged and washed 3 times with H_2O. The samples were placed in a vacuum oven overnight at 80°C. They were then submitted for SEM and XRD. 1:6:0 sample was submitted for BET

3.3.9ZIF-8 preparation in water + 1-MeIM at 80°C

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)	Yield (%)
1:3:0	148.6	440.3	0	113 (Not ZIF-8)
1:3:1	149.8	448.4	147.7	83
1:4:0	148.9	593.6	0	112 (Not ZIF-8)
1:4:2	148.7	593.0	294.3	68
1:6:3	148.0	887.6	453.0	59
1:10:5	147.6	1460.0	745.9	63

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 10ml H_2O. These were placed in the heating block at 80°C for 24 hours. These were centrifuged and washed 3 times with H_2O. They were placed in the vacuum oven overnight at 80°C. They were then submitted for SEM and XRD.

3.3.10 ZIF-8 preparation in water + 1-MeIM at 120°C

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)	Yield (%)
1:3:1	75.8	221.2	77.8	43
1:6:3	78.4	440.8	225	32

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 5ml H_2O. These were placed in Teflon lined stainless steel autoclaves and then placed in a conventional oven at 120°C for 24 hours. These were centrifuged and washed 3 times with H_2O. They were then submitted for SEM and XRD.

3.3.11 ZIF-8 preparation in water + 1-MeIM at 120°C

Ratio Zn:2MeIM:1MeIM	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)	Yield (%)
1:4:0	74.4	305.6	0	57
1:4:2	75.1	304.2	154.3	58

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 5ml H_2O. These were placed in Teflon lined stainless steel autoclaves and then placed in a conventional oven at 120°C for 24 hours. These were centrifuged and washed 3 times with H_2O. These samples were placed in the vacuum oven overnight at 80°C. They were then submitted for SEM and XRD.

3.3.12 ZIF-8 preparation in H_2O – Parallel reactions 1:20:20 (RT), 1:3:0 (RT), 1:3:0 (80°C), 1:6:0 (80°C), 1:6:0 (120°C)

1:20:20, 1:3:0 (both), 1:6:0(80°C) - A 20x solution of $Zn(NO_3)_2.6H_2O$ in water was made up by dissolving 2.9664 g $Zn(NO_3)_2.H_2O$ in 20 ml H_2O. This was separated into 20 equal amounts, 5x4 different parallel reactions.

1:6:0(120°C) - A 3x solution of $Zn(NO_3)_2.6H_2O$ in water was made up by dissolving 236.7 mg $Zn(NO_3)_2.H_2O$ in 3 ml H_2O. This was separated into 3 equal amounts 3 parallel reactions.

1:20:20- A 5x solution of 2MeIM and 1-MeIM in H_2O was prepared by dissolving 14.8124 g 2-MeIM and 14.8395 g 1-MeIM in 75 ml H_2O. This was separated into 5 equal amounts and added to 5 of the Zn solutions.

1:3:0 (RT and 80°C)- A 10x solution of 2MeIM in H_2O was prepared by dissolving 4.4301 g 2-MeIM in 100 ml H_2O. This was separated into 10 equal amounts and added to 10 of the Zn solutions.

1:6:0 (80°C) - A 5x solution of 2MeIM in H_2O was prepared by dissolving 4.4771 g 2-MeIM in 50 ml H_2O. This was separated into 5 equal amounts and added to 5 of the Zn solutions.

1:6:0 (120°C) - A 3x solution of 2MeIM in H_2O was prepared by dissolving 1.3770 g 2-MeIM in 15 ml H_2O. This was separated into 3 equal amounts and added to the 3 Zn solutions.

The 5x 1:20:20 and 5x 1:3:0 (RT) solutions were left stirring for 24 hours. The 5x 1:3:0 (80°C) and 5x 1:6:0 (80°C) solutions were placed in the heating block at 80°C for 24 hours. The 3x 1:6:0 (120°C) solutions were placed in Teflon lined stainless steel autoclaves and left for 24 hours in a conventional oven at 120°C. These were all centrifuged and washed 3 times with H_2O.

Chapter 4- Preparation of ZIF/Polymer composites

4.1 Traditional methods of composite preparation

Crystalline microporous metal-organic frameworks (MOFs) prepared using well-established principles of coordination chemistry are a versatile platform for a range of applications. Some of these applications are gas storage and gas separation, catalysis, drug delivery, other biomedical applications such as imaging and also sensor materials. This is due to their attractive structures and interesting properties such as low density structures, facile preparation, tuneable pore sizes and dimensions, high surface areas, ease of functionalization, and many others. However, the insoluble micron-sized crystals which are obtained by using the traditional methods of MOF synthesis are not ideal for these applications.[56] Due to this there is an increasing amount of research going into making MOF thin-films, nanoparticles and composite materials.[37, 73] To enhance their properties and processability for use in specific applications, MOFs need to be processed and made into appropriate structures with the correct functionalities and strengths depending on the particular properties required. To achieve a desired functionality from a material it is vital to adjust, augment, improve and change the properties of the surface so as to get the optical, electrical, biological or catalytic properties that the materials may need.[74] Due to this there is an increasing amount of research going into manipulating the size and shape of MOF crystals to optimize the physical properties and there is also focus on making MOF thin-films, nanoparticles and composite materials.[37, 73, 74]

MOF thin films and membranes are attractive for applications such as catalytic coatings, optoelectronics, gas separation, chemical sensors as well as smart membranes.[74] These materials allow new scope for the ability to functionalize surfaces and they can consist of free standing MOF films or can be on a support. These materials also allow the properties of the MOFs to be enhanced as the strong bond to a rigid support can allow for their use in applications not previously accessible to MOF powders.[74] MOFs are good materials for this application as they have a very high porosity and this is often hierarchical, with micro- meso and macropores all present in the particles. These pores can be loaded with some substrate depending on the desired property of the material being prepared. This loading will instil the material will the correct functionality for its desired application, e.g. dyes, molecular magnets or metallic nanoparticles could be loaded into the MOF pores to give them attractive properties. There have been several synthetic routes to preparing these materials one of which has been

used in the preparation of zeolite thin films for quite some time. This is the direct deposition of zeolite powder particles from a colloidal suspension onto a surface by spin-coating. [75] This method allows for the deposition of a very thin porous layer on various supports, as long as they are planar, using a colloidal suspension. The thickness of the deposited layer can be controlled by carrying out single or multiple spin-coating cycles and there is a certain level of control over the orientation of the deposited particles. The disadvantage is that the particles are not rigidly bound to the substrate surface as the interaction is not a covalent one. This method has been used for MOFs and milder conditions are possible which makes the deposition much easier. The MOF synthesis mixture can be used directly and the MOFs grow as they are deposited.[76] Other methods have also been adopted e.g. depositing pre-formed MOF nanoparticles, stepwise layer-by-layer growth onto the substrate, electrochemical deposition and deposition using a gel-layer approach. The approach taken depends on the material onto which the MOF is being deposited and each method has its advantages and disadvantages. One of the most interesting of these types of materials is the free-standing monolithic MOF thin films which can be used for membranes for applications such as gas separation. This is because they can be used for applications where supported MOFs may not be suitable for instance, if the support was not compatible with the system being used.

The preparation of composite materials is the method we focused on. Composites are multicomponent materials made up of different phases. They combine the properties of the different components which allows for tuning of the properties of the different phases. MOF-composite materials are made up of the MOF supported on some type of surface through surface interactions between functional groups. This area of research is growing very quickly with many different methods of composite preparation being explored. These are prepared in order to make the MOFs easier to handle and make them much more readily integrated into systems for applications such as gas storage, gas separation, catalysis or biomedical applications. The support gives the MOF more stability and makes them more appropriate for some applications, such as catalysis, where the catalyst needs to be recovered after the reaction. [8] In MOF composites the MOF is the dispersed phase and it is dispersed throughout a matrix which can be either organic or inorganic. There are several types of MOF-composite including monoliths, membranes, fibers and beads. MOF-polymer composites in particular are a way of enhancing the properties and processability of MOFs. Composite materials can come in the

form of many different structures including nanowires, microwire networks, nanofilms, and composite networks.

The desire to produce structures with directional, aligned pores means that new synthetic procedures have to be devised to allow for the formation of these types of structures for applications such as organic electronics, microfluidics and tissue engineering.[77]

A review written by Darren Bradshaw[56] focuses mostly on MOFs grown/deposited on 2- or 3-dimensional substrates using "top-down" and "bottom-up" approaches. The purpose of their review is to organise the currently reported MOF-composite materials into interface type to show the diversity of these materials as related to applications.[56]

One method of forming these MOF-composite materials is to take a monolith of the continuous phase and treating it with a reaction mixture of MOF and place it under solvothermal conditions. This causes the MOF crystals to grow throughout the monolith.[78] This has been done by Schwab et al[78] (2009) with a commercially available polymer monolith and HKUST-1 crystals were grown throughout the monolith structure. This gave a hierarchically porous "lung-like" structure.

The MOF-composites can also be prepared in a two-step process, whereby the MOF is first synthesised and is then subsequently deposited into a monolith structure.

MOF-composite membranes have also been prepared using commercially available polymers. The preformed MOF is dispersed homogenously throughout the polymer solution via sonication and then the composite membrane is formed by evaporation of the solvent. This has been done for several well-known MOFs including ZIF-8 and MOF-5.[79, 80] There is the disadvantage of these composites that the material becomes quite weak at high loadings of MOF and also the permeability of gases into the material decreases with increased loading.[80] To improve the quality of the membranes the MOFs can be pre-treated with a silylating agent e.g. N-methyl-N-(trimethylsilyl)trifluoroacetamide. [81]

Polymer fibres have also been used as the continuous phase for MOF-composite materials, with the composite preparation being achieved through electrospinning. [82] Electrospinning is a "top-down" approach to composite preparation and has been used to produce nanofibers from many materials, however to make these polymeric nanofibers porous, there is a need to prepare composite MOF-polymer nanofibers to combine the properties of both types of materials and get a hierarchically porous structure. The process consists of pre-formed MOF being dispersed

in a polymer solution. This solution is then concentrated and fed through a metallic needle by a syringe pump and collected on aluminium foil with a voltage applied. The diameter of these fibres can be controlled by the concentration of solution used and therefore this controls the properties of the composite fibers formed. This has been carried out by Ostermann et al[82] (2010) who formed ZIF-8/PVP (polyvinylpyrrolidone) composite nanofibers. They carried out XRD measurements on the samples before and after composite preparation and found that the ZIF-8 crystal structure is preserved during the composite preparation. This is very attractive for applications such as gas storage and gas separation. The use of different polymers could change the properties and strengths of the composite nanofibers and make them appropriate for different uses.

Polymer beads can also be used to produce MOF/polymer composite materials. These composites were first envisaged with the aim to increase the mechanical stability and to increase the ease of handling of the MOFs. This has been done in two ways, firstly by immersing the beads in a reaction mixture and forming the MOF by solvothermal synthesis, and secondly is the soaking of the beads in a pre-formed MOF suspension. [8, 40] Zhang et al[40] (2010) prepared hierarchically porous MOF/PAM (polyacrylamide) beads. They were both macro- and microporous and the degree of microporosity could be tuned by altering the MOF loading of the beads. These MOF/PAM beads showed increased stability over bulk phase MOF in heterogeneous reaction systems. They used both methods previously mentioned, the soaking in pre-formed MOF solution and also the solvothermal reaction in a Mother liquor. A problem with this type of composite material is that the MOF may only attach to the surface and therefore this limits the property enhancement.

4.2 Composites: Freeze drying

One novel method which can be used to produce composite materials is a procedure called Freeze drying or lyophilisation; this is the method we adopted and it allows 2D surface patterns or 3D monolithic compounds to be prepared. This is a very novel method of processing MOF/polymer composite materials. In the process the MOF crystallites are dispersed homogenously throughout the macropores of the polymer structure. This is with the aim to enhance the stability to mechanical erosion compared to bulk MOF phases. These composite materials could then be considered for use in several different applications including separation sciences and supported catalysis.

Freeze drying is a very simple process in which the solvent is crystallised in cryogenic solvents and then the frozen solvent is sublimed off at low pressure, going straight from the solid phase to the gas phase without entering the liquid phase. This gives a dry, solvent free material and allows the structure of the frozen compound to be retained and pores to be formed in the absence of the solvent molecules. Directional freezing is normally associated with polymer processing and has been used previously to create directionally porous materials however we will be applying it directly to colloidal MOFs dispersed in solutions of organic macromolecules and this has not yet been done. This allows a 'one pot' procedure to be used to process our MOF/polymer composite systems.

The process can produce all the composite structures previously mentioned including nanowires and composite networks and it does so without using any chemical reactions.[83] This means that there are no complications due to reactions between the framework material and the solvent, so a pure composite is produced. It is also a very cheap and simple method in comparison to some of the other methods used to produce aligned porous materials including microfabrication, soft lithography and photolithography.[77]

The solvent used can vary, and mixed solvents can be used, but they are mostly organic solvents and the most commonly used is water.[77] This again makes this procedure attractive over other methods as it makes it environmentally friendly, with only waste product being water, and it also allows these materials to be used for biomedical applications as water isn't harmful.[84]

Freeze drying consists of two stages, freezing and then drying. The solvent is directionally frozen in a bath of cryogenic liquid, e.g. liquid nitrogen, at a controlled rate. As the solution is lowered into the liquid nitrogen, the crystals grow from the bottom up, in one direction, forcing the particles and polymer molecules out of their path, aggregating between the ice crystals and forming directionally aligned pores. The crystallization of the solvent templates the aligned pore structure in the monolith and gives complex composite structures with a range of aligned pore architectures.[77] The crystallization is affected by a number of factors e.g. freezing rate, freezing temperature, solvent concentration, solvent type, solute used, and total time in the cryogenic liquid, and these change the size of the crystals formed.[84] Since the crystallization of the solvent crystals affects the pore architecture then changing any of these variables can give different porous structures.

This is followed by sublimation of the solvent under low pressure to produce the dried composite with an aligned macro- and mesoporous pore structure left by the solvent crystals. These structures are very attractive for use in applications such as stem cell growth and tissue engineering and also in the pharmaceutical industry to make more labile drugs.[85]

The effects of factors such as freezing temperature have been studied by various groups including Zhang et al in 2010, who studied how the freezing temperature would affect the size of the pores formed.[84] They found an increase in pore diameter when freezing temperature was increased when using a chitosan solution in acetic acid and in all cases very well aligned structures were produced.[84]

In this project we will prepare ZIF-8-polymer complexes by adopting this freeze drying method and then we will fully characterize the composite monoliths to allow them to be assessed for their applications.

4.3 Results and discussion

In the initial attempts, these ZIF-8 particles were prepared in methanol in a 1:8:1000 ratio Zn:2-MeIM:MeOH at room temperature for 16 hours. The particles were pure-phase ZIF-8 however they were very small nanoparticles of ~50 nm in diameter and were not easily visible in SEM images. These particles were dispersed homogenously throughout a 2wt% PVA solution via sonication.

The directional freezing method was initially carried out by hand, slowly lowering the samples into the bath of liquid nitrogen at ~1 mm every 10 seconds. This was with the aim to produce particles with directionally aligned porous structures as, by freezing in one direction, the ice grows in that direction, excluding the molecules in solution. The water is subsequently removed by freeze drying, which is a process whereby the solvent molecules are directly sublimed under vacuum from solid phase to gas phase therefore retaining the structure of the frozen monolith with the aligned pores.[84] The use of the freeze drying procedure is favourable over other methods for producing porous materials with water being used most commonly as the solvent making it an environmentally friendly route, and especially attractive when considering biological applications.. It avoids the use of large volumes of organic solvents which are generally needed in other routes e.g. electrospinning and emulsion templating, and it doesn't

require any time consuming washing after the process has been carried out. This is because there are no impurities brought into the compound when performing the freeze drying procedure, and therefore no further purification is required.[84] This processing technique has been used to produce porous polymers however, it is very novel in this area, having not been used for composite preparation until now.

The first sample, using the small ZIF-8 particles, seemed to shrink slightly in the freeze drier. The sample was then imaged by SEM and submitted for XRD measurements. The polymer structure was porous as can be seen in ***Figure 52***, where there is an aligned pore on the right hand side of the image. The ZIF-8 could not easily be seen in the structures although there does seem to be particles on the surface of the polymer in ***Figure 53***.

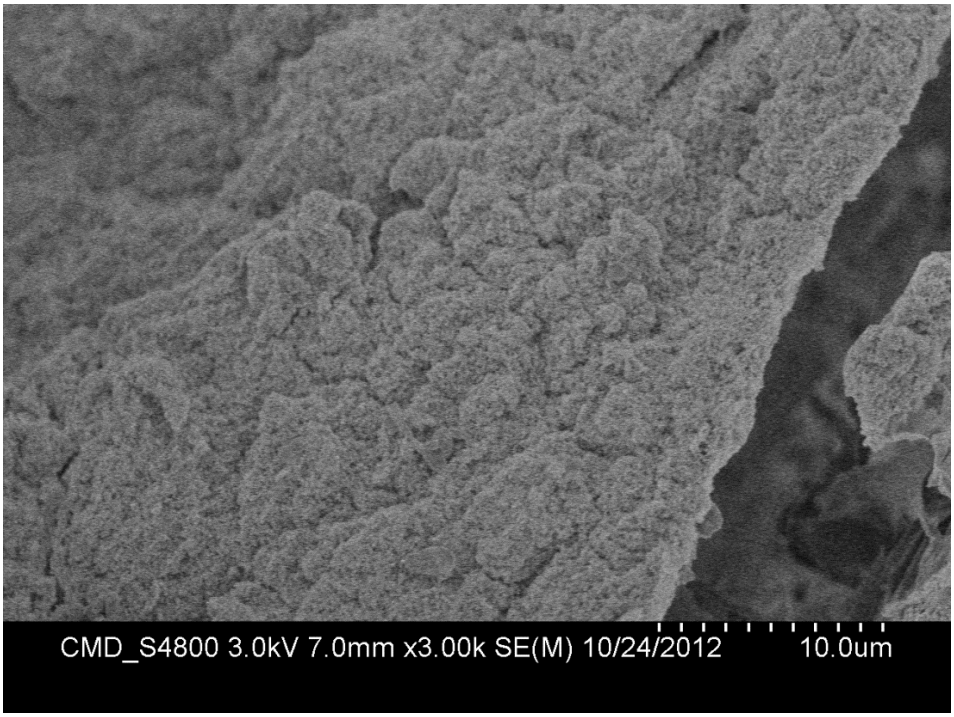


Figure 52*- ZIF-8@2wt%PVA composite with aligned pore visible on the right.*

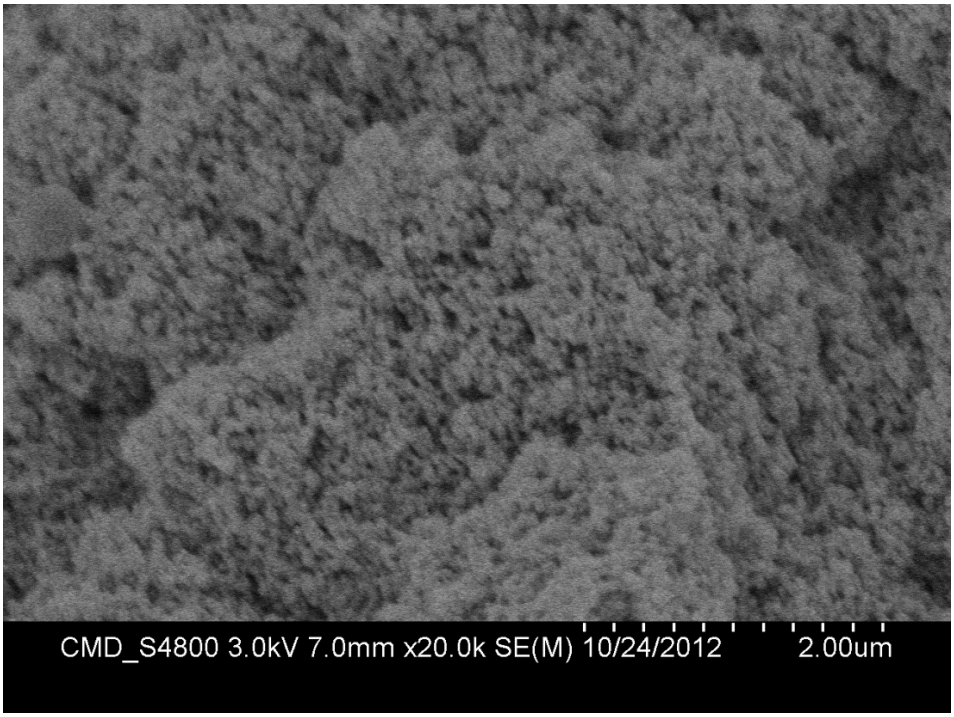


Figure 53*- ZIF-8@2wt%PVA composite with ZIF-8 just visible on the surface.*

This was what we thought would be the case when we originally synthesised these ZIF-8 particles, that they would prove unsuitable for the ZIF-8/polymer complexes due to their very small size making them hard to image via SEM, and undefined shapes.

We also tried to make the composites using a solution containing surfactant, to investigate whether this would make the structures more attractive with more aligned pores. The surfactants sodium dodecyl sulphate (SDS) and hexacetyltrimethylammonium bromide (CTAB) were used in a 0.5wt% solution made up from the 2wt% PVA solution. The samples again shrank in the freeze drier and the ZIF-8 was still very hard to see in the polymer structures. There was however an improvement in the structure of the monolith containing SDS, with the structure showing very aligned pores and very uniform structure. This is due to the anionic nature of the SDS surfactant interacting with the positive surface charge of ZIF-8 and creating a very uniform and controlled structure.[86]

The aligned porous structure of this SDS containing ZIF-8/PVA composite can be seen in ***Figure 54***.

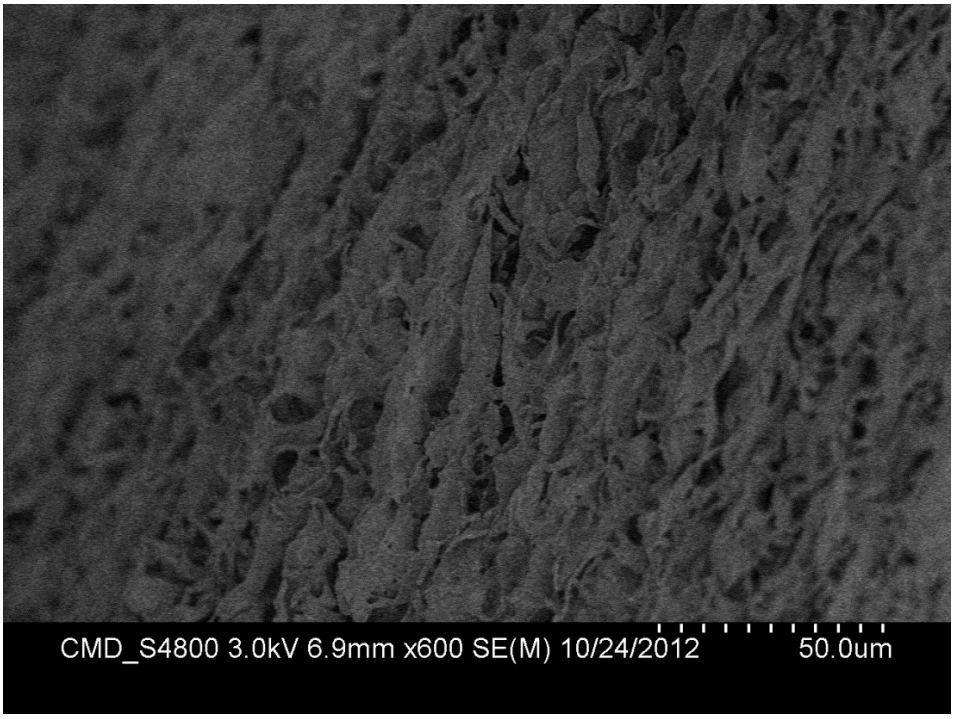


***Figure 54**- Aligned structure due to presence of SDS surfactant*

We had been using dry ZIF-8 which had been prepared washed and then dried in the vacuum oven at elevated temperatures. These particles may have been aggregating in the polymer solution and therefore not forming homogenous dispersions throughout the PVA solution. This is what we think was happening in these composites prepared with dry ZIF-8 and the reason why the ZIF-8 is not visible in the polymer structure. We decided to use wet ZIF-8 that is still in a very small volume of solvent after washing as this will not aggregate and will be more readily dispersed in the PVA solution, making it easier to get successful images of the composites.

The method we used to prepare the ZIF-8 was the same as before but the wet ZIF-8, rather than the dried ZIF-8, was used for the composite preparation. Five different reactions were set up, varying the amount of starting materials in order to produce the correct amount of ZIF-8 for using in the preparation of composites with ratios of ZIF-8:polymer of 1:1, 2:1 and 3:1 as well as 2:1 with CTAB and 2:1 with SDS in the polymer solution. The samples were prepared as before and directionally frozen in liquid nitrogen but after checking the freeze drier after 30 minutes the samples seemed to have melted although the shelf temperature was below -10°C.

The samples were looked at by SEM but the structures were no longer aligned due to the melting of the solutions.

The samples were prepared a further 4 times, with the exception of the ones containing surfactant which were not studied any further. In all cases the samples were observed to melt in the freeze drier even on the final attempt, where the maximum amount of MeOH possible was removed, soaking up the final amount with tissue paper before dispersing the ZIF-8 in the PVA solution. This is very unusual as the freeze drier shelf temperature was well below 0°C and therefore the water based samples shouldn't be melting.

To investigate this, throughout these repetitions, the samples were first left in the liquid nitrogen for an extended period of time, to see whether the reduction of temperature to the 77K for a longer period would keep the samples frozen long enough for the freeze dryer to remove the frozen solvent. This did not have the desired effect as the samples still melted. The removal of the methanol using tissue paper which was mentioned before was carried out because it was thought that the presence of the methanol could be increasing the melting point of the solution, with methanol having a melting point of -97°C which is obviously much lower than that of water. This however still did not stop the samples from melting and therefore the presence of the methanol was thought not to be the reason for the melting of the samples.

Another possibility for the cause of the melting of the composite samples is that the ZIF-8 that we used was so small. The particles were only approximately 50 nm in diameter. And it has been found that smaller particles can reduce the melting point of the solution.[87] This is a phenomenon that is not seen in bulk materials and is increasingly apparent as the size of the particles reduces. The effect has been attributed to the much lower surface to volume ratio of these nanoscale materials compared to their corresponding bulk materials and this alters their thermal and thermodynamic properties dramatically.[87-89]

We decided to investigate a different polymer while we were waiting for this to work, so we chose a natural polymer called chitosan to make into composite materials with our ZIF-8. We tried using the small ZIF-8 particles for our preliminary studies as we had some remaining. The wet ZIF-8 was used again and the 1wt% chitosan solution was added to the ZIF-8 in a glass sample vial. Immediately on addition of the chitosan solution to the ZIF-8 a gel formed. This was not something we had seen before with the PVA solution and we were not expecting it to happen. Other members of our research group had investigated the formation of silica/chitosan

composites and due to the fact that the NH_2-functionalized silica microspheres used, and ZIF-8 both have positive surface charges, we thought that this system would work equally as well.[90]

To investigate what was happening we first tested to see whether the addition of the two solutions had been too fast, so the wet ZIF-8 was added drop-wise to the chitosan solution with stirring to try to get a homogenous dispersion of ZIF-8 throughout the chitosan solution. This however still formed a gel even after stirring for 30 minutes.

The dry ZIF-8 was tried next, to see whether the presence of the methanol was affecting the solution in some way. The dry ZIF-8 was added slowly with stirring to the chitosan solution however a gel again formed straight away on addition of the particles to the solution. We then tried adding methanol to the chitosan solution and this did not form a gel so the methanol was clearly not the reason for the gel formation.

We thought that there could possibly have been some residual starting material present in the ZIF-8 which was causing the formation of this gel. We therefore tried adding the 2-MeIM to the chitosan solution and a gel did form. So we decided to wash the ZIF-8 more times with MeOH before adding to the chitosan solution to ensure that all the 2-MeIM was removed. However, on addition of the ZIF-8 to the chitosan, after washing 6 times with MeOH to ensure all the 2-MeIM was removed, a gel again formed.

The chitosan solution requires a very small amount of acid, 60µl acetic acid, to be added in order to allow the chitosan to be soluble in water. This very small amount of acid is what was causing the problem, as ZIF-8 is not stable in acidic solutions. The ZIF-8 framework was breaking down immediately on contact with the acidic solution, and releasing the 2-MeIM into the solution which then caused the formation of the gel. This system is clearly not compatible and therefore no further work on these ZIF-8/chitosan composites was carried out.

We decided to try the ZIF-8@PVA composite preparation again but this time using larger ZIF-8 particles prepared in the presence of the auxiliary ligand sodium formate. These particles were of nice defined particle sizes and much larger than those prepared by the original method. The ZIF-8 samples used were the ½, ¼, and 1/8 sodium formate samples. They did melt slightly but not fully in the freeze drier, therefore it is thought that both the methanol and the particle size were affecting the previous composites prepared. The ½ sodium formate sample did not show the ZIF-8 very effectively in the structure.

The ¼ and 1/8 samples showed the ZIF-8 in the structure and they also had nice structures. This can be seen by looking at ***Figure 55*** which shows the ¼ sodium formate ZIF-8/PVA composite sample.

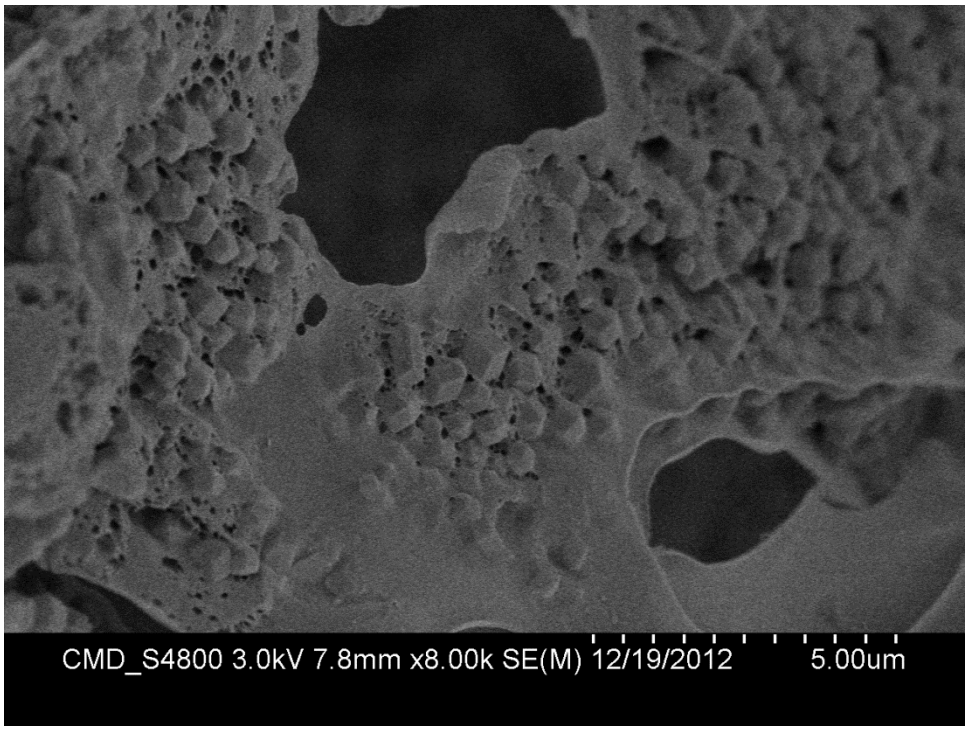


Figure 55*- ZIF-8@2wt%PVA + 1/4 Sodium formate. ZIF-8 particles clearly visible in the polymer structure.*

The pores can also be seen but from the images taken it could not be confirmed whether they had aligned structures. But, although these composites had better structures and more visible ZIF-8 particles in their frameworks, they still did melt slightly in the freeze dryer and therefore we decided to try the preparation of the composites using ZIF-8 that had been prepared in water as the freeze dryer did not seem to be working properly with these samples.

The ZIF-8 in water (1:20 Zn:2-MeIM, Room temperature) was used next to see whether the use of water and also the use of larger particles which in this case were approximately 300 nm in diameter which is much larger than the 50 nm particles prepared in methanol, and therefore shouldn't produce the same effect of reducing the melting point of the solution.

This composite material produced has very nicely aligned pores and the ZIF-8 is visible in the structure. This can be seen in ***Figure 56*** which shows the aligned pores structure and the ZIF-8 in the framework respectively.

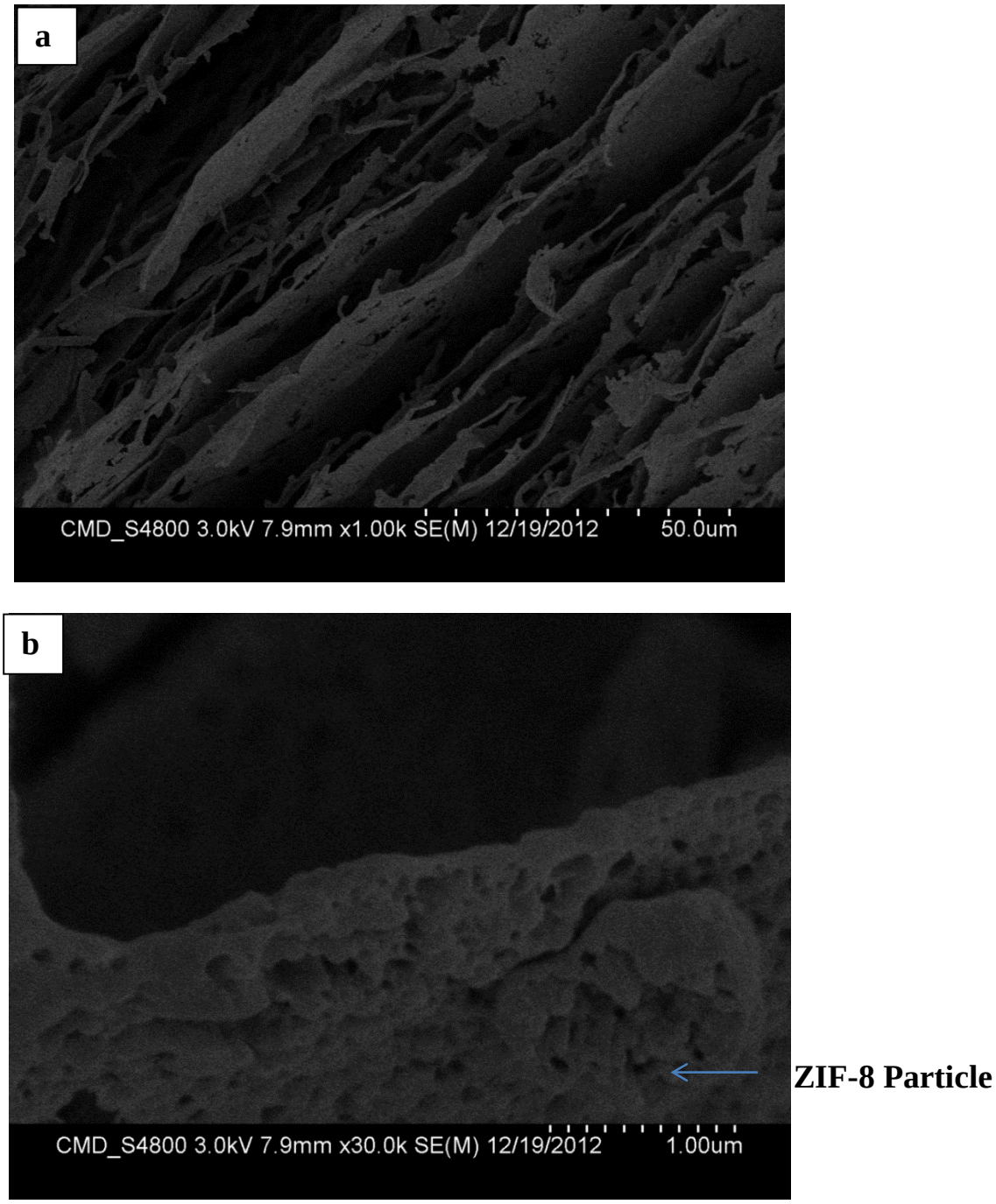


Figure 56*-Aligned porous structure of composite prepared with ZIF-8 1:20, water, RT, with ZIF-8 clearly visible in structure.*

It can clearly be seen that this composite preparation, using ZIF-8 prepared in water and of larger particle size, has been successful and has produced nicely aligned structures. The use of

ZIF-8 synthesised in water was decided to be the best route forward in preparation of the composites as it seems to, straight away, have produced a much better result.

From our work on synthesising attractive ZIF-8 particles of good morphologies and particle sizes for our needs, we chose three ZIF-8 conditions. These were Zn:2-MeIM:1-MeIM in water, 1:20:20 room temperature, 1:3:1 80°C and 1:10:2 80°C. These particles were chosen because of their particularly well-formed particles with interesting or well-defined particle morphologies.

We also decided to use a different polymer, polystyrene sulphonate (PSS), as this is known to produce very nicely aligned and ordered structures when directionally frozen. We used a 5wt% solution of PSS which had been used by a previous member of our group in another study and had produced very nice structures. We decided, for each of the ZIF-8 conditions chosen, to make these different composites with different ratios of ZIF-8:polymer, these were 1:1, 1:3 and 3:1.

The first ZIF-8 condition used for composite preparation was the 1:20:20 Zn:2-MeIM:1-MeIM at room temperature in water. The 1:20:20 ZIF-8 particles were chosen as they were nicely monodisperse with well-defined particle sizes and morphologies, shown in the SEM image in ***Figure 57***. They had particles of ~ 300 nm in diameter which was decided to be a good size for visualization of the particles in the polymer structure and still making the suspensions relatively stable.

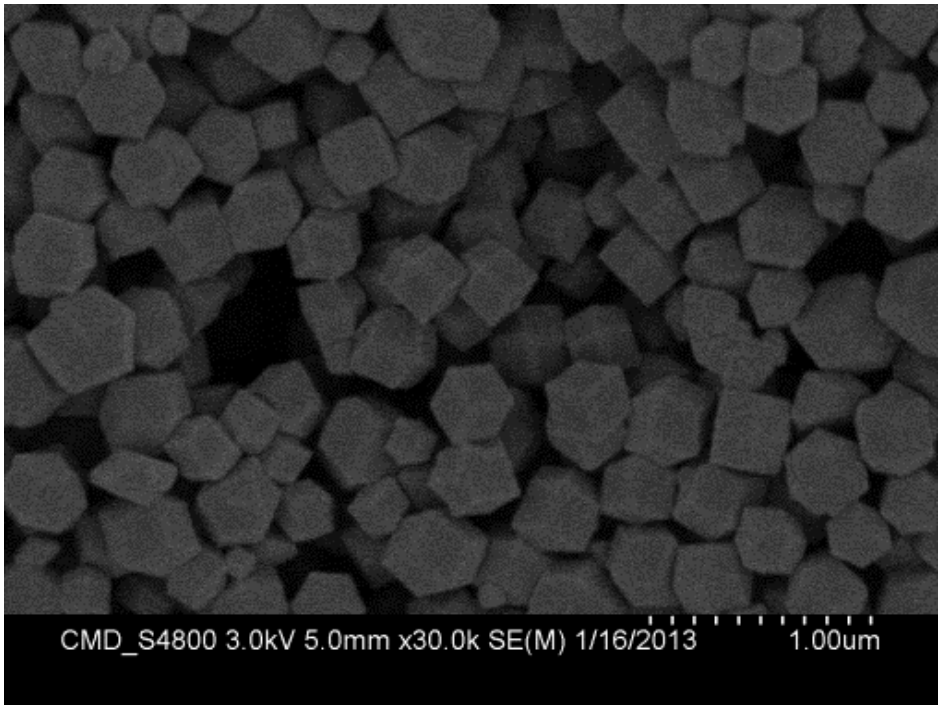


***Figure 57**- ZIF-8 prepared in water with 1-MeIM (1:20:20, room temperature)*

The SEM images of the composites show very nice structures with the ZIF-8 clearly visible in the polymer framework. The 1:1 ZIF-8 :PSS composite can be seen in ***Figure 58***, with a very aligned porous structure with the ZIF-8 visibly dispersed throughout.

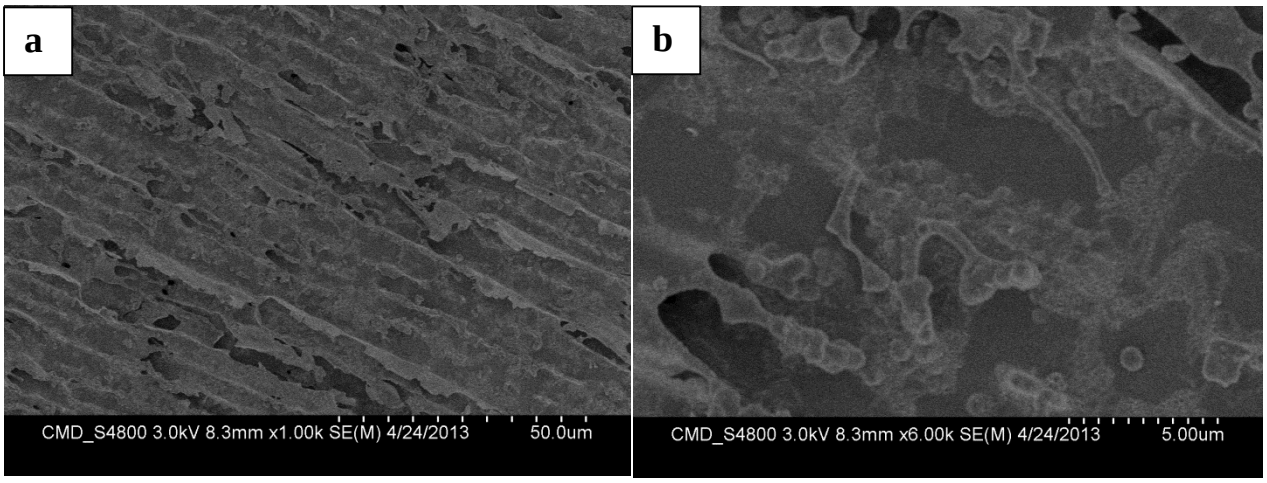


***Figure 58**- ZIF-8@5wt%PSS composite (1:20:20, RT) 1:1 ZIF:PSS - Very nicely aligned porous structure with ZIF-8 particles visible in the polymer framework.*

It can be seen straight away that these structures are much more aligned, with directional pores, than were the previous composites prepared in PVA solutions. It is also an advantage that the ZIF-8 can be seen in the structure

The 1:3 composite again showed very nicely aligned, directional pores with the ZIF-8 clearly visible in the structure. This is very positive as the polymer is in excess of the ZIF-8 and yet the ZIF-8 can still be seen clearly in the images. The structure of this composite can be seen in ***Figure 59***, where the SEM image on the right clearly shows ZIF-8 particles in the framework structure.

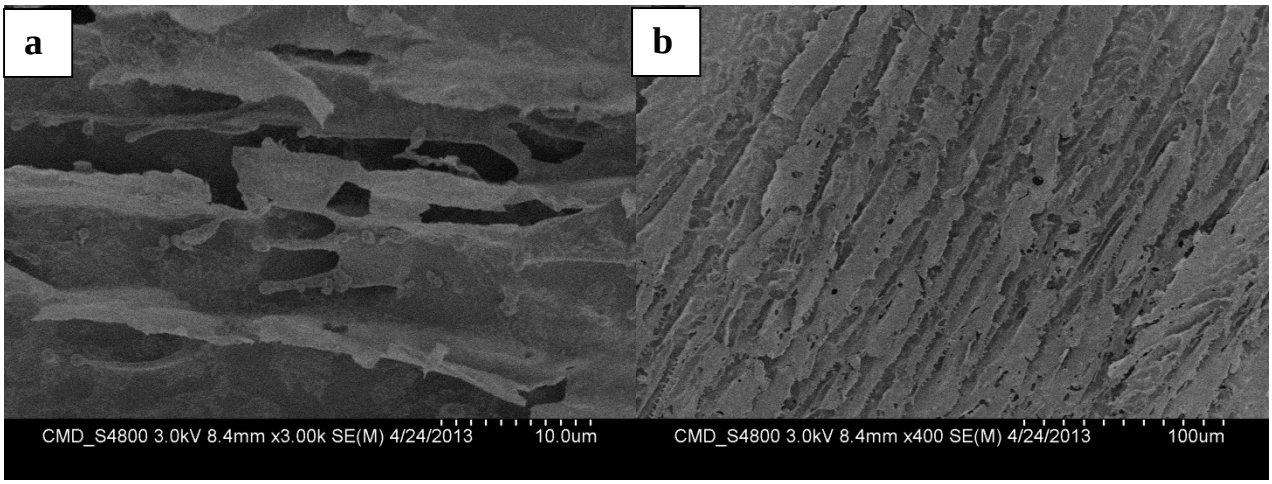


Figure 59*- ZIF-8@5wt%PSS composite (1:20:20, RT) 1:3 ZIF:PSS*

The 3:1 composite also had very nice aligned structures with the pores all having formed in one direction (***Figure 60***).

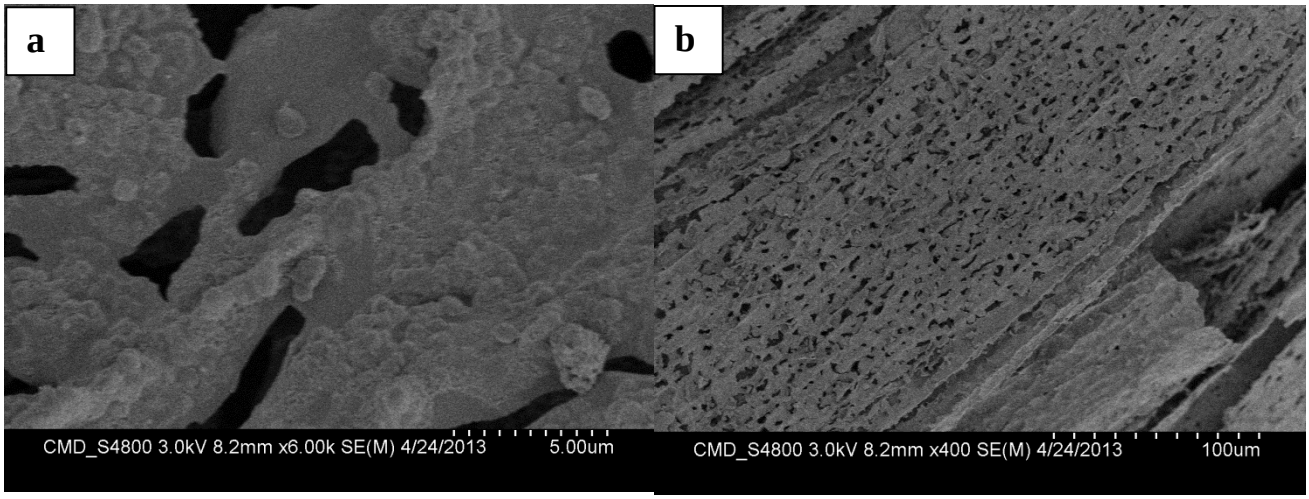


Figure 60*- ZIF-8@5wt%PSS (1:20:20, RT) 3:1.*

In this case it can be seen that there is a much larger amount of ZIF-8 in the framework which should mean that this structure has the highest surface area of all three 1:20:20 composite materials.

These composites were further characterised by Brunauer-Emmett-Teller Surface area measurements giving a N_2 adsorption isotherm which can tell us the surface area of the particles and also the pore size and volumes. The surface area measurement can also be used to determine an accurate ratio of ZIF-8:polymer if the surface area of the ZIF is known as well.

The surface area of the ZIF-8 particles prepared under the conditions 1:20:20 Zn:2-MeIM:1-MeIM at room temperature and in water as the solvent was 1681 m^2g^{-1}. This means that these particles are highly porous and will be useful for many applications in which MOFs are desired. The value of 1681 m^2g^{-1} is a typical value for ZIF-8 particles that are microporous but usually when they're prepared under solvothermal conditions. Our value is significantly higher than has been reported in most papers in which the syntheses have been done at room temperature.[70] For example, Venna et al, in their synthesis of ZIF-8 in methanol, found a BET surface area of only ~700 m^2g^{-1} at 100% crystallinity of their ZIF-8 particles.[62] Another example is the work by Pan et al[26] (2011) where they report a BET surface area of ~ 1000 m^2g^{-1} which they say is typical of room temperature syntheses.[60, 91] The N_2 adsorption isotherm for these particles is shown below in ***Figure 61.***

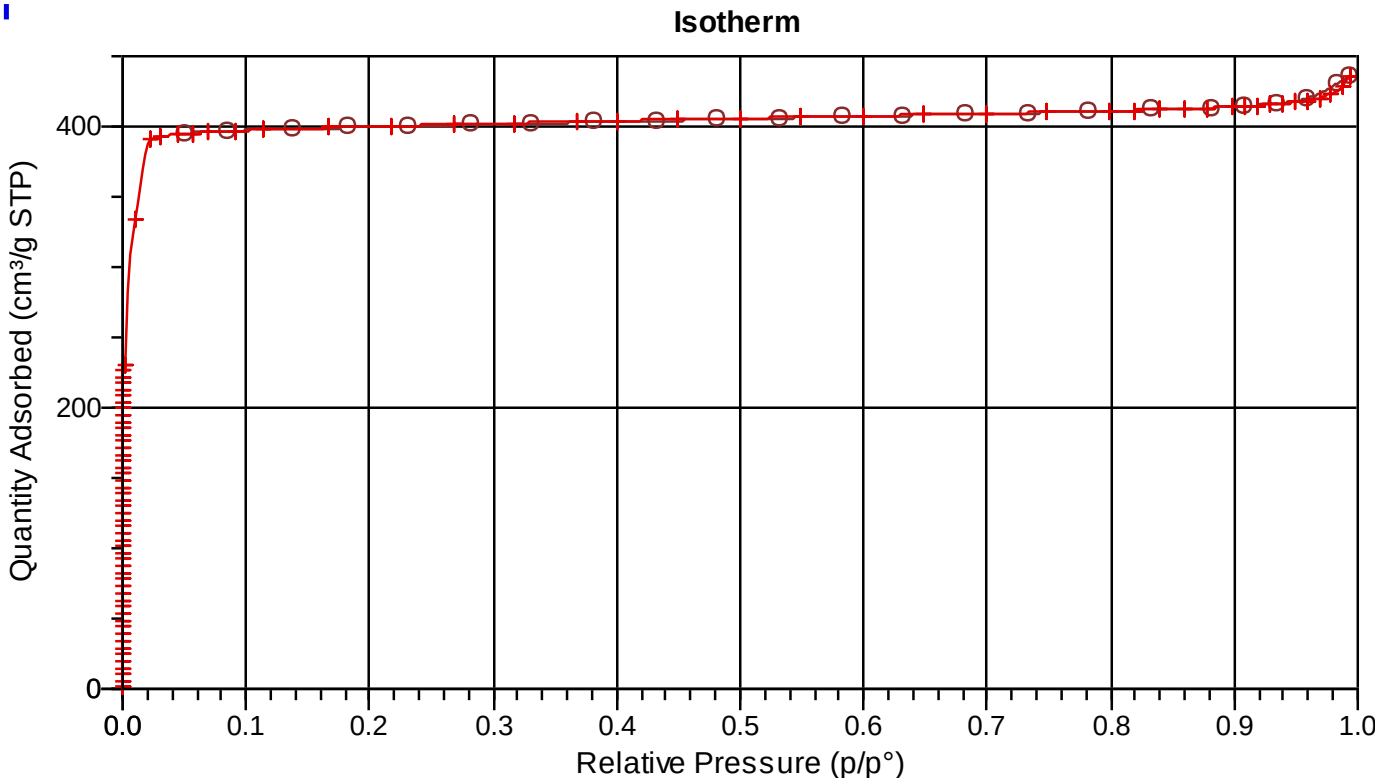


Figure 61- *N_2 adsorption isotherm for ZIF-8 +1-MeIM 1:20:20, RT, water*

This is a Type I nitrogen adsorption isotherm and it shows that these ZIF-8 particles are microporous. From the isotherm data, we also can calculate the pore volume and median pore size and these are 0.67 cm^3g^{-1} and 0.83 nm respectively. This confirms that the particles are microporous. The BJH average pore size however is 6.3 nm which means that there must be mesopores present in these ZIF-8 particles making them hierarchically porous. There must be a much larger proportion of the micropores however, as there is no hysteresis loop on the Nitrogen adsorption isotherm.

The three composites had much lower BET surface areas with the values varying depending on the proportion of ZIF-8 to polymer was used in the preparation of the composites.

The 1:3 had the lowest BET surface area, which is what would be expected as it has the least amount of the porous ZIF-8 present in the structure. This material had a BET surface area of only 96 m^2g^{-1}. This is relatively low however, as can be seen from the N_2 adsorption isotherm below (***Figure 62***), there is a hysteresis loop starting to appear, which indicates the presence of mesopores probably caused by the presence of a larger proportion of the polymer than of the

ZIF-8. The mesopores are caused by spaces between the polymer and the ZIF-8. This means that we have successfully prepared a hierarchically porous, directionally aligned monolith which has a uniform structure.

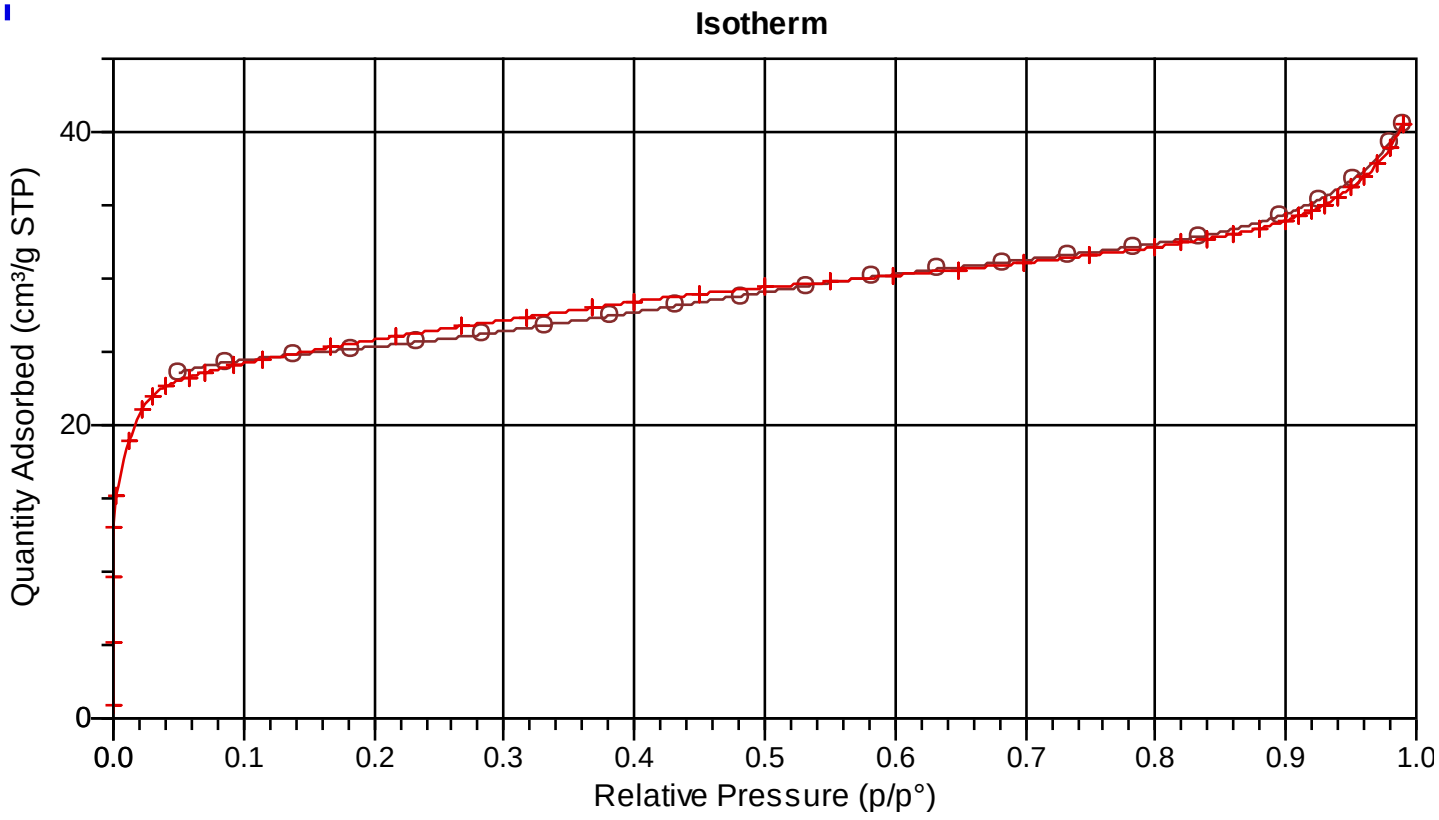


***Figure 62**- N_2 adsorption isotherm for ZIF-8@5wt%PSS 1:3 (1:20:20, RT, water)*

The pore volume and median pore size for this composite were 0.06 cm^3g^{-1} and 0.85 nm with the BJH average pore width at 4.89 nm. This shows that there are both micro- (<2 nm diameter) and mesopores (>2 nm but <50 nm) present in this composite material and with its very attractive, aligned structure it will be useful for many different applications.

The 1:1 ZIF-8@PSS composite had a BET surface area of 205 m^2g^{-1} which is more than double that of the 1:3 composite as would be expected. There is an even proportion of ZIF-8 to polymer so therefore the highly porous ZIF-8 is having more of an effect and increasing the surface area. The N_2 adsorption isotherm for this composite material is shown below (***Figure 63***) and, as can be seen, there is a hysteresis loop appearing again. This shows that our composite material is hierarchically porous.

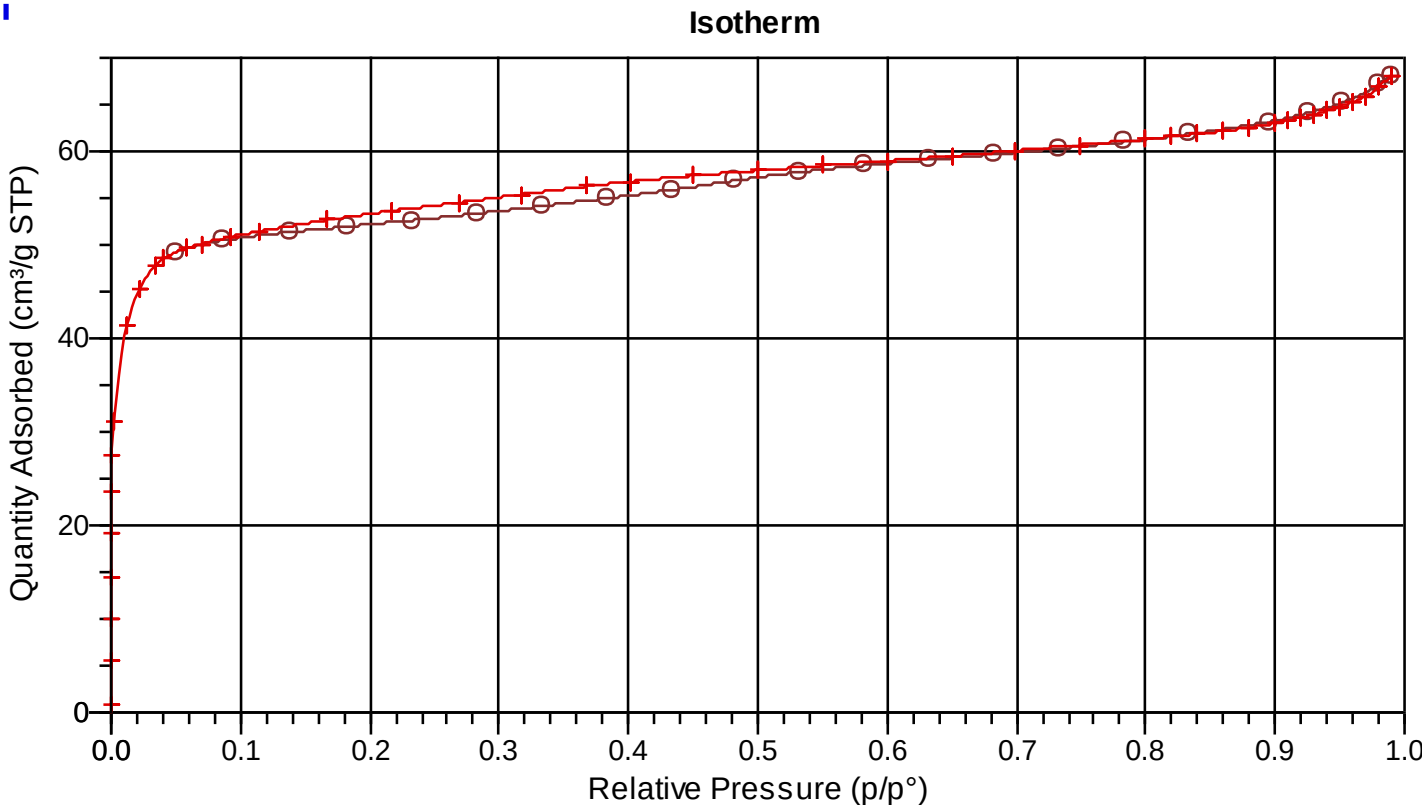


***Figure 63**- N_2 adsorption isotherm for ZIF-8@5wt%PSS 1:1 (1:20:20, RT, water)*

The pore volume and median pore size for this composite were 0.10 cm^3g^{-1} and 0.84 nm with the BJH average pore width at 4.06 nm. This shows that yet again, there are both micro- and mesopores present in this composite material making it hierarchically porous, and with its very attractive, aligned structure it will be useful for many different applications including catalysis, gas storage and separation and drug delivery.

The 3:1 ZIF-8@PSS composite had a BET surface area of 440 m^2g^{-1} which is more than double that of the 1:1 composite as would be expected. There is now an excess of ZIF-8 to the polymer so therefore the highly porous ZIF-8 is having more of an effect and increasing the surface area. The N_2 adsorption isotherm for this composite material is shown below (***Figure 64***) and, as can be seen, the hysteresis loop appearing earlier is much less apparent here with a more Type I isotherm appearing. This is because the ZIF-8 is more predominantly microporous and this microporosity is having a more marked effect with the presence of more ZIF-8 than PSS.

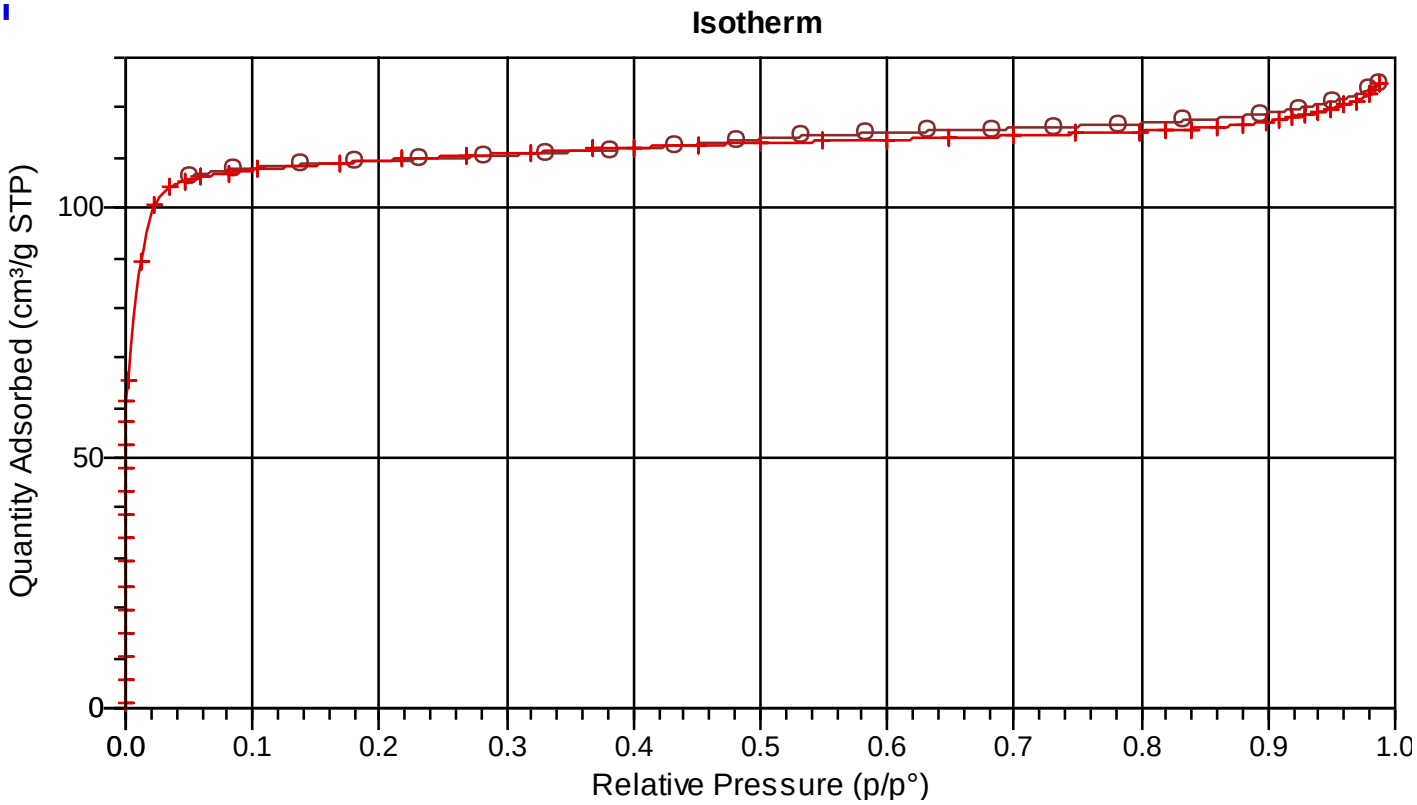


***Figure 64**- N_2 adsorption isotherm for ZIF-8@5wt%PSS 3:1 (1:20:20, RT, water)*

The pore volume and median pore size for this composite were 0.19 cm^3g^{-1} and 0.83 nm with the BJH average pore width at 4.57 nm. This shows that yet again, there are both micro- and mesopores present in this composite material making it hierarchically porous although this is less apparent from the nitrogen adsorption isotherm in this case however it is still a hierarchically porous material.

The most obvious difference between these three composites, other than the BET surface areas, is the pore volumes of the materials. The pore volume is very low for the composite with the least ZIF-8 present indicating that the pores may be becoming blocked by the polymer and also that there are less mesopores which have a larger pore volume. But this value increases as the amount of ZIF-8 in the composite increases and this increase is in conjunction with the increase in BET surface area. This makes sense as an increase in the total volume of the pores will increase the surface area of the materials and allow more uptake of nitrogen in the BET measurements.

The second ZIF-8 condition used for composite preparation was the 1:10:2 Zn:2-MeIM:1-MeIM at 80°C in water. The 1:10:2 ZIF-8 particles were chosen as they were nicely monodisperse with well-defined particle sizes and morphologies, shown in the SEM image in ***Figure 65***. They had particles of ~ 400 nm in diameter.

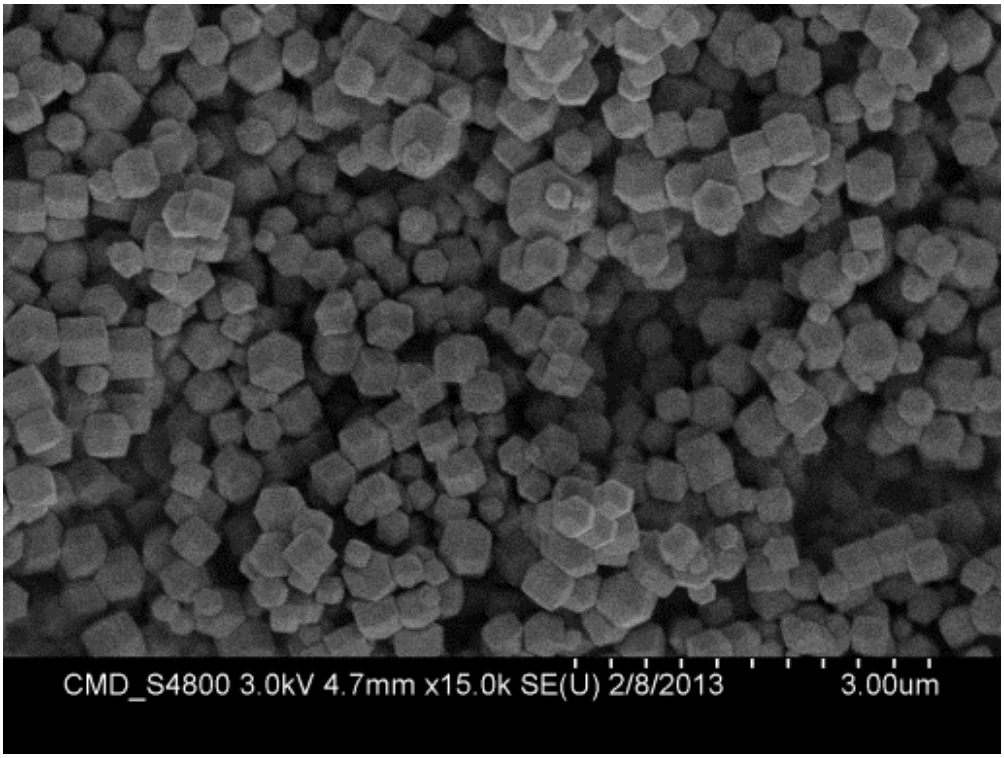


Figure 65*- ZIF-8 prepared in water with 1-MeIM (1:10:2, 80°C)*

The SEM images of the composites show very nice structures with the ZIF-8 clearly visible in the polymer framework. The 1:1 ZIF-8 :PSS composite can be seen in ***Figure 66***, with aligned porous structure with the ZIF-8 visibly dispersed throughout.

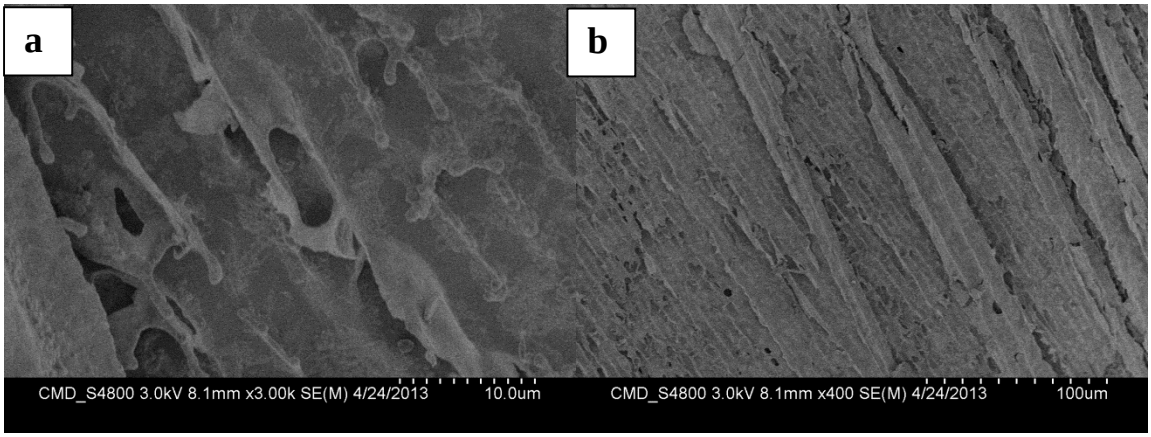


Figure 66*- ZIF-8@5wt%PSS composite (1:10:2, 80°C) 1:1 ZIF:PSS - Very nicely aligned porous structure with ZIF-8 particles visible in the polymer framework.*

It can again, as for the case with the 1:20:20 ZIF-8 composites, be seen straight away that these structures are much more aligned, with directional pores, than were the previous composites prepared in PVA solutions. The ZIF-8 is not quite as visible although this could just be due simply to the sample preparation for the SEM imaging. The left hand picture in Figure 76 shows some ZIF-8 particles in the structure and the right hand picture shows the incredibly aligned and directional structure of this porous material.

The 1:3 composite again showed very nicely aligned, directional pores with the ZIF-8 clearly visible in the structure. This is again very good as the polymer is in excess of the ZIF-8 and yet the ZIF-8 can still be seen clearly in the images. The structure of this composite can be seen in ***Figure 67***, where the SEM image on the right clearly shows ZIF-8 particles in the framework structure. Both images in ***Figure 67*** show that this composite has a very well-aligned structure with the pores all having grown in one direction only.

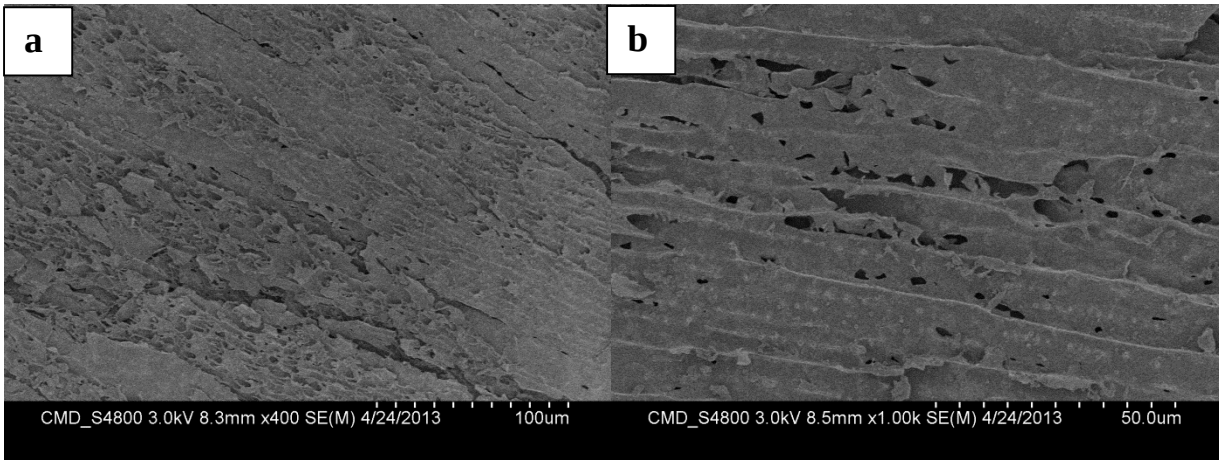


***Figure 67**- ZIF-8@5wt%PSS composite (1:10:2, 80°C) 1:3 ZIF:PSS*

The 3:1 composite also had very nice aligned structures with the pores all having formed in one direction (***Figure 68***).

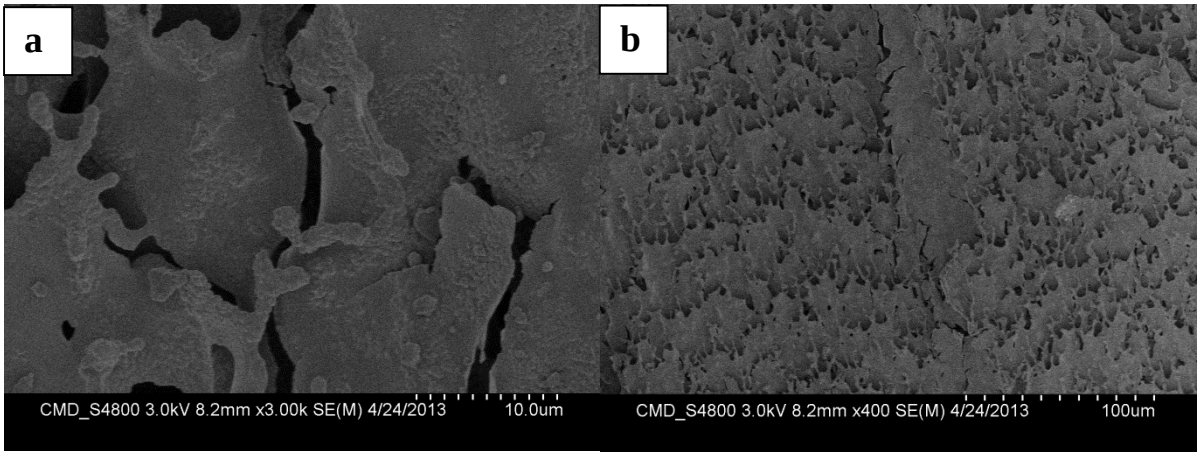


***Figure 68**- ZIF-8@5wt%PSS (1:10:2, 80°C) 3:1.*

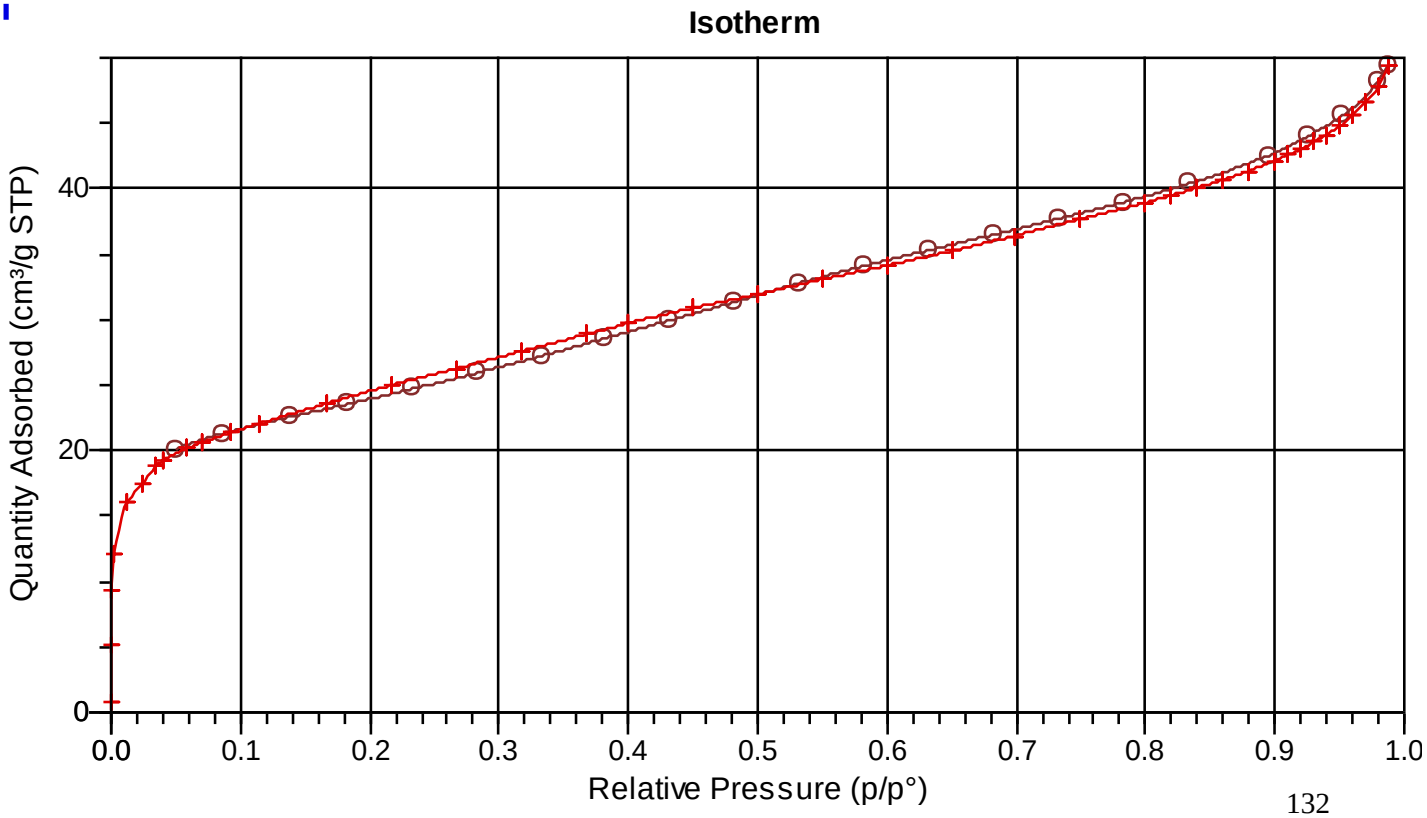
In this case it can be seen that there is a much larger amount of ZIF-8 in the framework, with it being quite densely packing in the structure, which should mean that this structure has the highest surface area of all three 1:10:2 composite materials.

These composites were further characterised by Brunauer-Emmett-Teller Surface area measurements giving a N_2 adsorption isotherm which can tell us the surface area of the particles

and also the pore size and volumes. The surface area measurement can also be used to determine an accurate ratio of ZIF-8:polymer if the surface area of the ZIF is known as well.

These three composites had very similar BET surface areas to the 1:20:20 cases, with the values varying depending on the proportion of ZIF-8 to polymer that was used in the preparation of the composites.

The 1:3 had the lowest BET surface area, just as was the case for the 1:20:20 composites, which is what would be expected as it has the least amount of the porous ZIF-8 present in the structure. This material had a BET surface area of only 86 m^2g^{-1}. This is relatively low, even lower than was seen for the composites prepared using the 1:20:20 ZIF-8 particles. However, as can be seen from the N_2 adsorption isotherm below (***Figure 69***), the isotherm is starting to take the shape of a Type II adsorption isotherm, which is most commonly caused due to the presence of pores that are larger than micropores or with a large distribution of pore sizes. This indicates the presence of mesopores probably caused by the presence of a larger proportion of the polymer than of the ZIF-8 but it could also mean that this ZIF-8 has larger pores or that the micropores are blocked by residual starting materials. As ZIFs are typically microporous in nature we can assume that these micropores are also present and therefore this data means that we've produced hierarchically porous monoliths with very aligned and directional porous structures.



The pore volume and median pore size for this composite were 0.07 cm^3g^{-1} and 0.87 nm with

Figure 69*- N_2 adsorption isotherm for ZIF-8@5wt%PSS 1:3 (1:10:2, 80°C, water)*

are both micro- (<2 nm diameter) and mesopores (>2 nm but <50 nm) present in this composite material and with its very attractive, aligned structure it will be useful for many different applications including gas separation and storage and also catalysis. This is because, if there is a Type I, II or IV adsorption isotherm, then the material can be used efficiently for the separation of gases.

The 1:1 ZIF-8@PSS composite had a BET surface area of 232 m^2g^{-1} which is almost triple that of the 1:3 composite as would be expected. There is an even proportion of ZIF-8 to polymer so therefore the highly porous ZIF-8 is having more of an effect and increasing the surface area. The N_2 adsorption isotherm for this composite material is shown below (***Figure 70***) and, as can be seen, there is now a hysteresis loop appearing, as was the case for the 1:20:20 composite materials. This shows that this composite material definitely contains mesopores but also, due to the Type I shape of the isotherm, there must also be micropores. This means our composite is hierarchically porous.

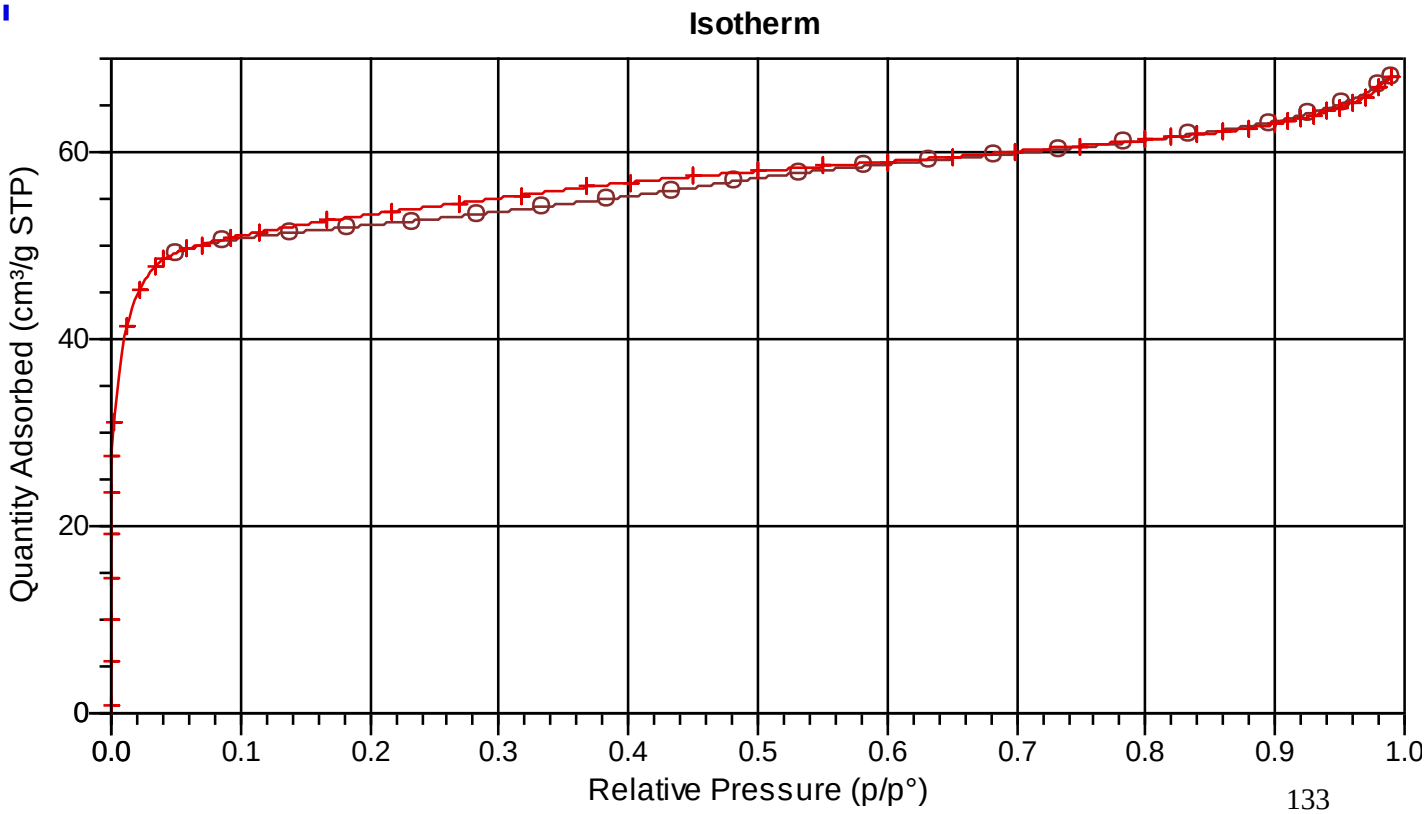


***Figure 70**- N_2 adsorption isotherm for ZIF-8@5wt%PSS 1:1 (1:10:2, 80°C, water)*

The pore volume and median pore size for this composite were 0.13 cm^3g^{-1} and 0.84 nm with the BJH average pore width at 4.20 nm. This shows that yet again, there are both micro- and mesopores present in this composite material making it hierarchically porous, and with its very attractive, aligned structure it will be useful for many different applications.

The 3:1 ZIF-8@PSS composite had a BET surface area of 521 m^2g^{-1} which is more than double that of the 1:1 composite as would be expected. There is now an excess of ZIF-8 to the polymer so therefore the highly porous ZIF-8 is having more of an effect and increasing the surface area. The N_2 adsorption isotherm for this composite material is shown below (***Figure 71***) and, as can be seen, the hysteresis loop appearing earlier is much less apparent here with an even more pronounced Type I isotherm appearing. This is because the ZIF-8 is more predominantly microporous and this microporosity is having a more marked effect with the presence of more ZIF-8 than PSS.

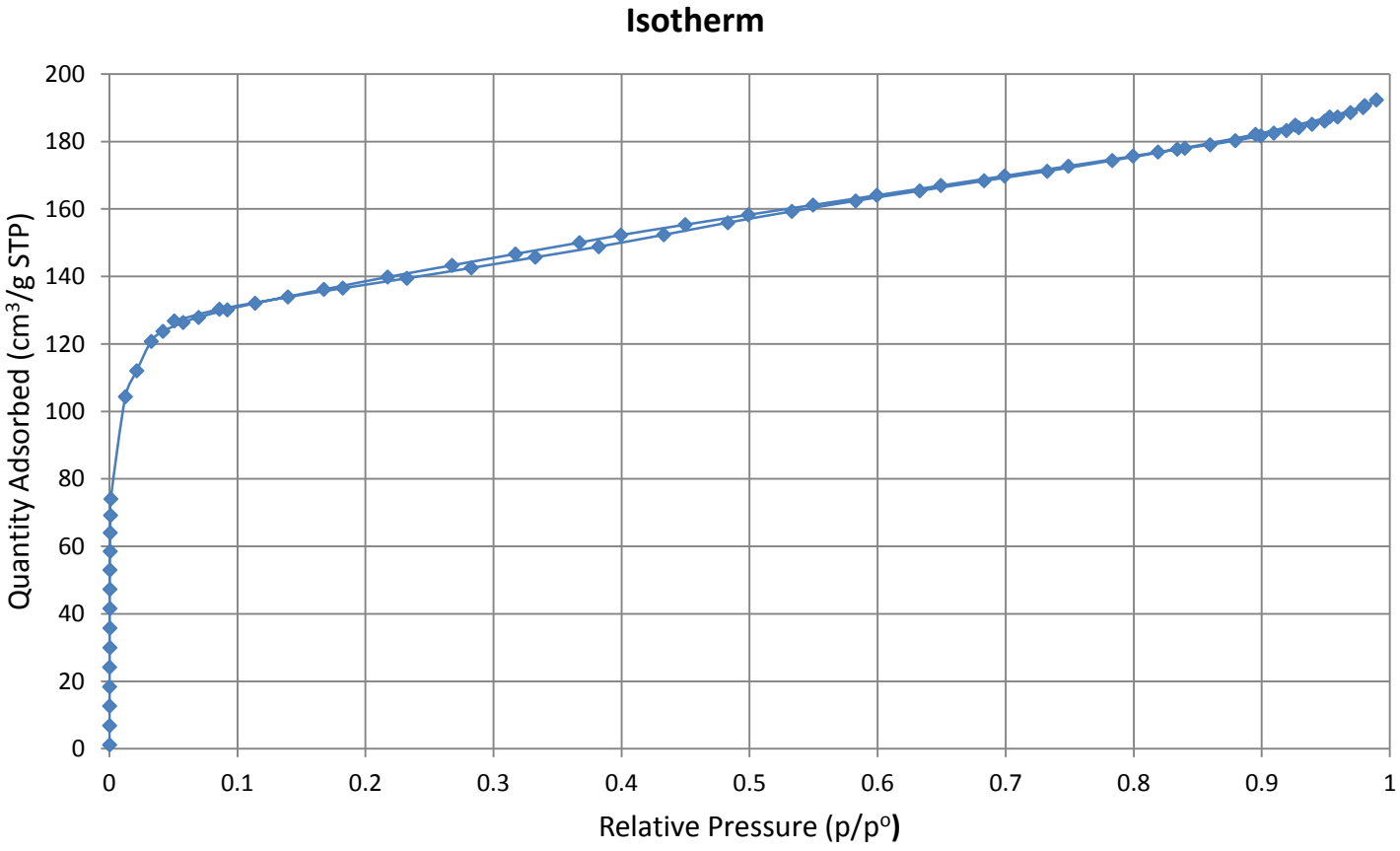


***Figure 71**- N_2 adsorption isotherm for ZIF-8@5wt%PSS 3:1 (1:10:2, 80°C, water)*

The pore volume and median pore size for this composite were 0.30 cm^3g^{-1} and 0.84 nm with the BJH average pore width at 3.92 nm. This shows that yet again, there are both micro- and mesopores present in this composite material making it hierarchically porous although this is less apparent from the nitrogen adsorption isotherm in this case however it is still a hierarchically porous material. The BJH average pore size value is smaller than in the 1:20:20 composite and also that was in any of the previous composites discussed. This means that the pores in this composite are much more predominantly microporous and therefore the presence earlier in the 1:3 composite of the Type II isotherm may have been due to the small amount of ZIF-8 present, rather than the ZIF-8 being mesoporous.

Similarly to the 1:20:20 case, the most obvious difference between these three composites, other than the BET surface areas, is the pore volumes of the materials. The pore volume is very low for the composite with the least ZIF-8 present indicating that the pores may be becoming blocked by the polymer and also that there are less mesopores which have a larger pore volume. But this value increases as the amount of ZIF-8 in the composite increases and this increase is in conjunction with the increase in BET surface area. This makes sense as an increase in the total volume of the pores will increase the surface area of the materials and allow more uptake of nitrogen in the BET measurements.

In both of these two composites they seem to give very well-defined, aligned, directionally porous structures with very precise control over the BET surface area, pore volume and pore size distribution depending on the ratio of the ZIF-8:PSS. When comparing these two composites, the ZIF-8@5wt%PSS with the 1:10:2 ZIF-8 particles appear to give the best control and the most aligned structures, with the properties of the composites varying quite dramatically on variation of the ratio of ZIF-8:PSS. This means that the precise properties needed in the material will be able to be chosen and the properties will be able to be tuned to the particular needs of the application.

The last ZIF-8 condition we used to prepare the composite materials were the 1:3:1 Zn:2-MeIM:1-MeIM at 80°C in water. These were very interesting particles which seemed to form nano-aggregates to give ~2 µm sized ZIF-8 particles. This can be seen in ***Figure 72.***

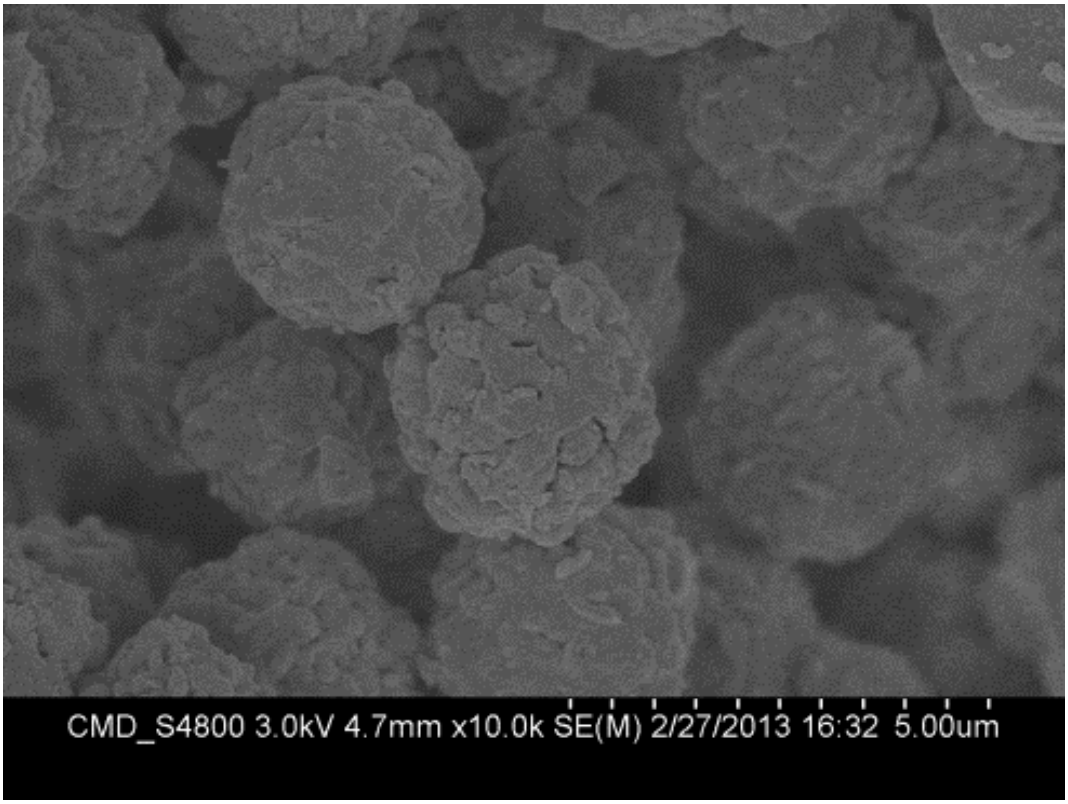


Figure 72*- ZIF-8 1:3:1 80°C in water.*

We used the same method to prepare these composites, trying to control the ratio of ZIF-8:PSS quite accurately. The only problem we thought may happen when using these larger particles was that they could be much more difficult to disperse throughout the polymer solution and may start to "fall-out" of solution before the freezing could be carried out.

The SEM images of the composites show very nice structures with the ZIF-8 clearly visible in the polymer framework. The 1:1 ZIF-8 :PSS composite can be seen in ***Figure 73***, with very an aligned porous structure with the ZIF-8 visibly dispersed throughout. The aligned structure is identified by the fact that all the pores and lines in the structure go in one direction only.

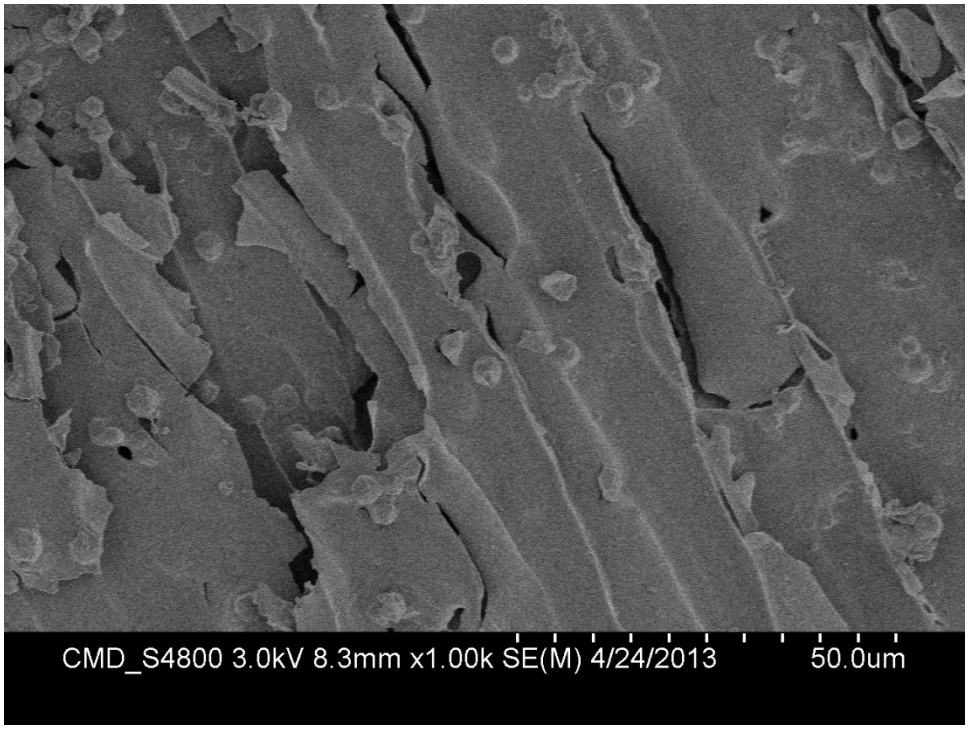


Figure 73- *ZIF-8@5wt%PSS composite (1:3:1, 80°C) 1:1 ZIF:PSS – Nicely aligned porous structure with ZIF-8 particles visible in the polymer framework.*

It can again be seen, as for the 1:20:20 and 1:10:2 ZIF-8 composites, that these structures are much more aligned, with directional pores, than were the previous composites prepared in PVA solutions. The ZIF-8 can also be seen in the structure especially clearly due to the large sizes of these nano-aggregate particles.

The 1:3 composite again showed a very nicely aligned, directional porous structure with the ZIF-8 clearly visible in the polymer framework. This is very positive seen as the polymer is in excess of the ZIF-8 and yet the ZIF-8 can still be seen clearly in the images. This is even more apparent than in the 1:20:20 case, due to the larger size of the ZIF-8 nano-aggregate particles. The structure of this composite can be seen in ***Figure 74***, where the SEM image shows both the aligned structure of the polymer composite as well as clearly showing the presence of ZIF-8 particles dispersed throughout the framework.

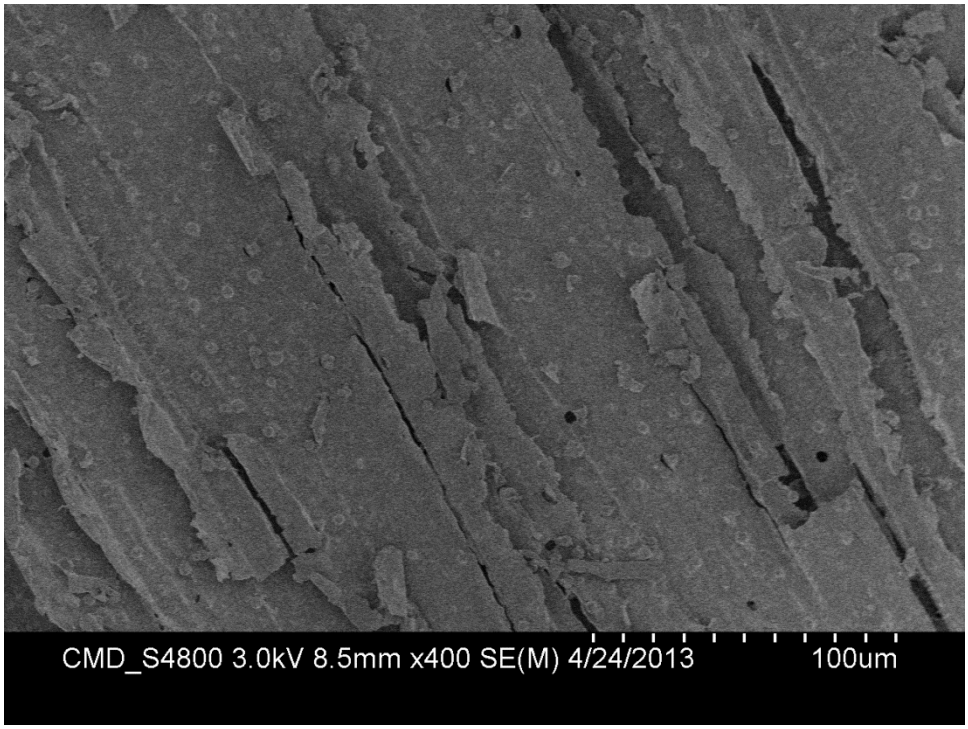


***Figure 74**- ZIF-8@5wt%PSS composite (1:3:1, 80°C) 1:3 ZIF:PSS*

The 3:1 composite also had an aligned structure although it is not as easily noticeable, but if we observe the SEM image in ***Figure 75*** we can see that the structure is aligned horizontally across the image with all the pores moving in this direction.

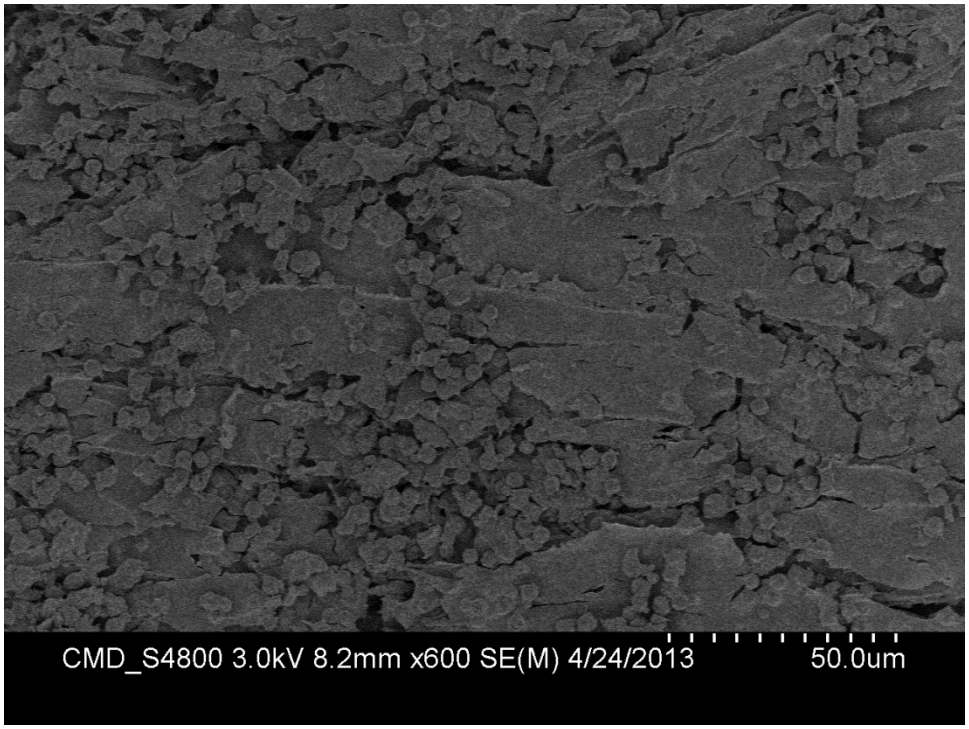


***Figure 75**- ZIF-8@5wt%PSS (1:3:1, 80°C) 3:1.*

In this case it can be seen that there is a much larger amount of ZIF-8 in the framework with the ZIF-8 being quite densely packed into the framework. These structures were determined not to be as attractive as the other composite materials prepared and therefore the surface area measurements were not taken.

4.4 Conclusion and Future work

In this project we have investigated different synthetic conditions in which to prepare ZIF-8 with the aim to control the particle size and morphology so as to tune the properties of the ZIF-8 samples for the needs of specific applications. These samples have been characterised in order to identify the most promising candidates for carrying on into the next stages of our study, composite preparation. We identified three ZIF-8 synthesis environments which we thought would produce different properties and types of composite materials due to their interesting morphologies and sizes. The three ZIF-8 samples chose were the Zn:2-MeIM:1-MeIM in water under the conditions: 1:20:20 at room temperature, 1:10:2 at 80°C and 1:3:1 at 80°C. These 3 ZIF-8 samples were used to continue our work further, by developing novel methods of

composite preparation. The composites prepared by the directional freezing and freeze drying method have been fully characterised and they all gave very well-defined, aligned, directionally porous materials with the ZIF-8 clearly visible in the polymer framework structure. The most interesting structures were achieved for the 1:20:20 and 1:10:2 samples with the 1:10:2 samples having the most aligned structures and also the most varying BET surface areas, pore volumes and pore diameters. This means that the properties of the composites will be very easy to control by simple changing the ratio of ZIF-8:PSS and this means these materials will be able to be tuned for their use in specific applications.

Further investigation into the ZIF-8 formation and particularly in water at slightly elevated temperatures possibly with the sodium formate auxiliary ligand instead of the 1-MeIM to see whether there is a different trend in results.

4.5 Experimental

4.5.1 Freeze casting 1: Synthesis of ZIF8@ 2%PVA composites (2:1)

2wt% PVA (8k-10k) solution was made up. 57.8mg dry ZIF-8 (**2.2.2**) was dispersed in 1.5ml of 2% PVA solution via sonication for 20 minutes to give a homogeneous dispersion. This was then directionally frozen in a bath of liquid nitrogen.

57.6mg dry ZIF-8 was added to 1.5ml 2wt% PVA solution and then sonicated for 20 minutes to give a homogenous dispersion. This was then put straight into the freezer.

A control sample of 1.5ml 2wt% PVA only was directionally frozen in liquid nitrogen.

A 0.5wt% CTAB solution was prepared by dissolving 50.2mg CTAB in 10ml of the 2wt% PVA solution. 57.7mg dry ZIF-8 was dispersed in 1.5ml of the CTAB/PVA solution by sonicating for 20 minutes. This was immediately directionally frozen in liquid nitrogen.

A 0.5wt% SDS solution was prepared by dissolving 50.2mg SDS in 10ml of the 2wt% PVA solution. 57.8mg dry ZIF-8 was dispersed in 1.5ml of the SDS/PVA solution by sonicating for 20 minutes. This was immediately directionally frozen in liquid nitrogen.

These five frozen samples were placed in the freeze dryer for 48 hours. SEM images and XRD spectra were obtained for the samples.

4.5.3 Freeze casting 3

1:1 ZIF:Polymer- 91.4mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 202.1mg 2MeIM in 12ml MeOH.

2:1- 183.5mg $Zn(NO_3)_2.6H_2O$ in 12 ml MeOH was added to 407.2mg 2MeIM in 12ml MeOH.

3:1- 275.6mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 606.9mg 2MeIM in 12 ml MeOH.

2:1 + CTAB- 183.8mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 405.8mg 2MeIM in 12ml MeOH.

2:1 + SDS- 183.7mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 407.8mg 2MeIM in 12ml MeOH.

These were all left for 16 hours stirring and then centrifuged and washed three times with MeOH.

The wet ZIF was added to 1.5ml 2wt% PVA solution. For the CTAB and SDS samples a 0.5wt% solution was prepared by dissolving 50.5mg CTAB and SDS respectively in 10ml 1.5wt% PVA solution and 2ml of this solution was used instead.

The ZIF-8 was dispersed homogeneously throughout the PVA solution by sonicating for 20 minutes and then the samples were directionally frozen in liquid nitrogen and placed in the freeze dryer for 48 hours. The samples melted in the freeze dryer.

4.5.4 Freeze casting 4: ZIF-8@Chitosan composites

1:1 ZIF:Chitosan- 90.42mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 202.0mg 2MeIM in 12ml MeOH.

2:1- 185.8mg $Zn(NO_3)_2.6H_2O$ in 12 ml MeOH was added to 407.2mg 2MeIM in 12ml MeOH.

3:1- 275.8mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 606.0mg 2MeIM in 12 ml MeOH.

2:1 + CTAB- 186.4mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 407.8mg 2MeIM in 12ml MeOH.

2:1 + SDS- 184.1mg $Zn(NO_3)_2.6H_2O$ in 12ml MeOH was added to 406.7mg 2MeIM in 12ml MeOH.

These were all left for 16 hours stirring and then centrifuged and washed three times with MeOH.

The wet ZIF was added to 1.5ml 1wt% Chitosan solution prepared by dissolving 2.0037g Chitosan in 200ml water and adding 600µl acetic acid. For the CTAB and SDS samples a 0.5wt% solution was prepared by dissolving 50.5mg CTAB and SDS respectively in 10ml 1wt% chitosan solution and 1.5ml of this solution was used instead. On addition of ZIF-8 to the chitosan solution a gel formed.

4.5.4.1Gelation tests

Wet ZIF-8 was added dropwise to the chitosan solution with stirring. A gel formed.

Dry ZIF-8 was added slowly to the chitosan solution with stirring. A gel still formed.

MeOH was added to the chitosan solution with stirring. No gel formed.

2MeIM was added to the chitosan solution. A gel formed.

4.5.5 ZIF-8@Chitosan composite

25ml of the ZIF-8 batch (**2.2.4**) was taken and centrifuged, washing 6 times with methanol. This was added slowly with stirring to 1.5ml of 1% chitosan solution, prepared by dissolving 2g chitosan in 200ml water with 600µl acetic acid. A gel formed.

2ml of ZIF-8 in MeOH was taken and was washed with water. A precipitate formed which went to the top of the centrifuge tube when centrifuged. This was submitted for XRD.

4.5.6 Freeze casting 5: ZIF-8@2% PVA composites

1:1 ZIF:Polymer - 12.5ml of the batch ZIF-8 (**2.2.4**) was taken and centrifuged, washing 3 times with MeOH. The MeOH was poured off and the wet ZIF-8 was dispersed in 1.5ml 2% PVA solution. This was sonicated for 15 minutes to give a homogenous dispersion. This was then directionally frozen in liquid nitrogen and placed in the freeze drier for 48 hours. This was repeated to give more sample for characterization.

2:1 ZIF:polymer- 25ml of the batch ZIF-8 was taken and centrifuged, washing 3 times with MeOH. The MeOH was poured off and the wet ZIF-8 was dispersed in 1.5ml 2% PVA solution. This was sonicated for 15 minutes to give a homogenous dispersion. This was then directionally

frozen in liquid nitrogen and placed in the freeze drier for 48 hours. This was repeated to give more sample for characterization.

3:1 ZIF:polymer- 37.5ml of the batch ZIF-8 was taken and centrifuged, washing 3 times with MeOH. The MeOH was poured off and the wet ZIF-8 was dispersed in 1.5ml 2% PVA solution. This was sonicated for 15 minutes to give a homogenous dispersion. This was then directionally frozen in liquid nitrogen and placed in the freeze drier for 48 hours. This was repeated to give more sample for characterization.

The repeated samples all melted in the freeze drier. These samples were refrozen in liquid nitrogen along with 1.5ml water and 1.5ml 2% PVA solution as controls. These were placed in the freezer to test whether the freezer was causing the melting.

The samples were prepared again and they melted in the freeze drier again.

4.5.7 ZIF-8@2% PVA composites

12.5ml of the ZIF-8 + ½, ¼, 1/8 sodium formate (**2.3.7**) and 4ml of ZIF-8 in water (**3.3.2**) were taken and centrifuged, washing 3 times with MeOH or water respectively. The solvent was poured off and the wet ZIF-8 was dispersed in 1.5ml 2% PVA solution. This was sonicated for 15 minutes to give a homogenous dispersion. This was then directionally frozen in liquid nitrogen and placed in the freeze drier for 48 hours. Bumped due to vacuum and MeOH samples melted after 30 minutes.

4.5.8 ZIF-8@2%PVA composite preparation- dry test

3ml 2% PVA solution was put in a glass vial and ~50mg dry ZIF-8 was added slowly with stirring. This was then sonicated for 15 minutes to disperse the ZIF-8. It was then directionally frozen in liquid nitrogen and placed in the freeze drier for 48 hours. This was submitted for SEM imaging.

4.5.9 ZIF-8 preparation in H_2O – 5 parallel reaction 1:20:20 (RT)

Ratio Zn:2MeIM:1MeIM 1:20:20	Mass Zn (mg)	Mass 2MeIM (g)	Mass 1-MeIM (mg)
1	148.6	2.9852	3.0394
2	149.6	2.9645	2.9849
3	148.5	2.9925	2.9817
4	149.9	2.9881	3.0047
5	149.5	2.9828	3.0490

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 15ml H_2O.They were stirred at room temperature for 24 hours. These were centrifuged and washed 3 times with H_2O.

4.5.9.1 ZIF-8@5wt%PSS composite preparation (1:20:20, H_2O, RT)

5wt% polystyrene sulphonate (PSS) was prepared by dissolving 5.0058g PSS in 100ml water.

Theoretical amounts needed:

ZIF:5wt%PSS	ZIF-8 (mg)	PSS (mg)
1:3	33.33	100
1:1	100	100
3:1	300	100

Amounts used:

ZIF-8:PSS	ZIF-8 (wet) (mg)	PSS
1:3	49.8	2ml
1:1	102.9	2ml
3:1	302.2	2ml

The wet ZIF-8 (1:20:20, H_2O, RT) was weighed out and 2ml of 5wt% PSS solution was added. This was sonicated for 15minutes to get a homogenous dispersion and then was directionally frozen in liquid nitrogen and placed in the freeze dryer for 48 hours.

4.5.10 ZIF-8 preparation in H_2O – 5 parallel reaction 1:3:1 (80°C)

Ratio Zn:2MeIM:1MeIM 1:3:1	Mass Zn (mg)	Mass 2MeIM (mg)	Mass 1-MeIM (mg)
1	148.0	444.2	146.8
2	149.4	446.5	160.2
3	150.6	444.7	140.1
4	149.3	444.4	146.6
5	150.3	446.2	179.2

$Zn(NO_3)_2.6H_2O$ was dissolved in 1ml H_2O and to this was added a solution of 2-MeIM and 1-MeIM in 10ml H_2O. These were placed in the heating block at 80°C for 24 hours. These were centrifuged and washed 3 times with H_2O.

4.3.10.1ZIF-8@5wt%PSS composite preparation (1:3:1, H_2O, 80°C)

ZIF-8:PSS	ZIF-8 (wet) (mg)	PSS
1:3	36.9	2ml
1:1	104.6	2ml
3:1	316.3	2ml

The wet ZIF-8 (1:3:1, H_2O, 80°C) was weighed out and 2ml of 5wt% PSS solution was added. This was sonicated for 15minutes to get a homogenous dispersion and then was directionally frozen in liquid nitrogen and placed in the freeze dryer for 48 hours.

4.5.11 ZIF-8 preparation in H_2O – 5 parallel reaction 1:10:2 (80°C)

A 5x solution of $Zn(NO_3)_2.6H_2O$ in water was made up by dissolving 748.4mg $Zn(NO_3)_2.6H_2O$ in 5ml H_2O. This was separated into 5 equal amounts. To each of these was added 10ml of a solution of a 5x solution of 2-MeIM and 1-MeIM made up by dissolving 7.4875g 2-MeIM and 1.496g 1-MeIM in 50ml water H_2O.They were placed in the heating block at 80°C for 24 hours. These were centrifuged and washed 3 times with H_2O.

4.5.11.1 ZIF-8@5wt%PSS composite preparation (1:10:2, H_2O, 80°C)

ZIF-8:PSS	ZIF-8 (wet) (mg)	PSS
1:3	46	2ml
1:1	105.2	2ml
3:1	303.9	2ml

The wet ZIF-8 (1:10:2, H_2O, 80°C) was weighed out and 2ml of 5wt% PSS solution was added. This was sonicated for 15minutes to get a homogenous dispersion and then was directionally frozen in liquid nitrogen and placed in the freeze dryer for 48 hours.

4.5.12 ZIF-8 preparation in H_2O – 5 parallel reactions 1:20:20 (RT), 1:3:1 (80°C), 1:10:2 (80°C)

A 15x solution of $Zn(NO_3)_2.6H_2O$ in water was made up by dissolving 2.2291g $Zn(NO_3)_2.6H_2O$ in 15ml H_2O. This was separated into 15 equal amounts.

1:20:20- A 5x solution of 2MeIM and 1-MeIM in H_2O was prepared by dissolving 14.8537g 2-MeIM and 14.8507g 1-MeIM in 75 ml H_2O. This was separated into 5 equal amounts and added to 5 of the Zn solutions.

1:3:1- A 5x solution of 2MeIM and 1-MeIM in H_2O was prepared by dissolving 2.2340g 2-MeIM and 750.4mg 1-MeIM in 50 ml H_2O. This was separated into 5 equal amounts and added to 5 of the Zn solutions.

1:10:2- A 5x solution of 2MeIM and 1-MeIM in H_2O was prepared by dissolving 7.4743g 2-MeIM and 1.4910g 1-MeIM in 50 ml H_2O. This was separated into 5 equal amounts and added to 5 of the Zn solutions.

The 5 1:20:20 solutions were left stirring for 24 hours. The 1:3:1 and 1:10:2 solutions were placed in the heating block at 80°C for 24 hours. These were all centrifuged and washed 3 times with H_2O.

4.5.12.1 ZIF-8@5wt%PSS composite preparation (1:20:20, H_2O, RT), (1:3:1, H_2O, 80°C), (1:10:2, H_2O, 80°C)

ZIF-8:PSS (1:20:20)	ZIF-8 (wet) (mg)	PSS
1:3	38.6	2ml
1:1	103.9	2ml
3:1	304.3	2ml

ZIF-8:PSS (1:3:1)	ZIF-8 (wet) (mg)	PSS
1:3	72.4 (very wet)	2ml
1:1	122.4 (very wet)	2ml
3:1	371.4 (very wet)	2ml

ZIF-8:PSS (1:10:2)	ZIF-8 (wet) (mg)	PSS
1:3	36	2ml
1:1	110.8	2ml
3:1	304.2	2ml

The wet ZIF-8 was weighed out and 2ml of 5wt% PSS solution was added. This was sonicated for 15minutes to get a homogenous dispersion and then was directionally frozen in liquid nitrogen and placed in the freeze dryer for 48 hours. These samples were submitted for XRD and SEM imaging. Samples were submitted for BET surface area determination although all attempts failed.

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